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(54) Title: THERMOPLASTIC POLYURETHANE COMPOSITIONS WITH SHAPE MEMORY PROPERTIES

(57) Abstract: A thermoplastic polyurethane composition having shape memory properties comprises the reaction product of a polyester polyol component comprising a short chain diol and a dicarboxylic acid, such as 2,5-furandicarboxylic acid, a diisocyanate component, and a chain extender component.



THERMOPLASTIC POLYURETHANE COMPOSITIONS WITH SHAPE MEMORY PROPERTIES

FIELD OF THE INVENTION

5 **[001]** The present invention relates to thermoplastic polyurethane (TPU) compositions with excellent shape memory and thermomechanical properties, which can be used for molded articles.

BACKGROUND OF THE INVENTION

10 **[002]** Thermoplastic polyurethanes (TPU) are an excellent choice of material for many applications owing to their easy processing and outstanding properties, including resistance to abrasion, impact and chemical agents, high flexibility and cut, good environmental weathering, and biocompatibility.

15 **[003]** As is well known, TPUs are prepared by reacting diisocyanate compounds, polymeric diols and difunctional chain extenders. Typically, high amounts of diisocyanate and chain extenders need to be employed to obtain products with high hardness that maintain the mechanical properties of the material. However, owing to the high toxicity and environmental impact of the diisocyanates, said high hardness materials present a high environmental footprint. Hence, the development of high hardness materials with limited amount of the hazardous diisocyanate is of special interest to manufacture more environmentally friendly TPUs.

20 **[004]** The development of thermally-induced shape memory polymers (SMPs) has gained attraction thanks to their added interest properties, such as recovery stress and energy output. These materials can switch from a plastic deformation behavior to an elastic one when triggered by an external stimulus, such as heat, light or electricity. 25 SMPs perform a mechanical work when the switch in deformation behavior occurs. In particular, heat activated SPMs, those that toggle between both behaviors upon reaching either a glass transition temperature (T_g) or a melting transition temperature (T_m), can be exploited for many applications in different fields, like in medical implants or devices, smart actuators or self-deploying structures.

30 **[005]** Shape memory polymers and molded articles are disclosed for instance in US2008221279A1 and US10907006B2.

[006] Nevertheless, there is still a general need in the state of the art of SMPs with less toxicity, high recovery stress and energy output. The present invention sets out to

meet some or all of the above-identified needs and to solve some or all of the above-identified problems.

SUMMARY OF THE INVENTION

[007] The invention relates to thermoplastic polyurethane compositions with shape memory properties.

[008] In one aspect, the invention relates to a thermoplastic polyurethane composition comprising the reaction product of:

(a) a polyester polyol comprising a short chain diol and a dicarboxylic acid selected from the group consisting of 2,5-furandicarboxylic acid.

(b) a diisocyanate component; and

(c) a chain extender component.

[009] The thermoplastic polyurethane compositions are suitable for manufacturing molded articles with shape memory properties.

[0010] In another aspect, the invention relates to a molded article comprising the thermoplastic polyurethane composition according to the first aspect.

[0011] The following embodiments of the present subject matter are contemplated:

[0012] 1. A thermoplastic polyurethane composition comprising the reaction product of: (a) a polyester polyol comprising a short chain diol and 2,5-furandicarboxylic acid; (b) a diisocyanate component; and (c) a chain extender component.

[0013] 2. The thermoplastic polyurethane composition according to embodiment 1, wherein the polyester polyol has a number average molecular weight lower than 5,000 Da.

[0014] 3. The thermoplastic polyurethane composition according to either embodiment 1 or embodiment 2, wherein the polyester polyol has a number average molecular weight in the range from 800 to 5,000 Da, preferably from 1,000 to 3,000 Da.

[0015] 4. The thermoplastic polyurethane composition according to any one of embodiments 1 to 3, wherein the diisocyanate is in an amount to provide a NCO:OH molar ratio of from 1:1.25 to 1.25:1.

[0016] 5. The thermoplastic polyurethane composition according to any one of embodiments 1 to 4, wherein the molar ratio of chain extender to polyol is from 1:1 to 1:9.

[0017] 6. The thermoplastic polyurethane composition according to any one of embodiments 1 to 5, wherein the molar ratio of 2,5-furandicarboxylic acid to short chain

diol of the polyester polyol (a) is from 1:1 to 1:5 or 1:1 to 1:2, or 1:1 to 1:1.5, or 1:1 to 1:1.25.

[0018] 7. The thermoplastic polyurethane composition according to any one of embodiments 1 to 6, wherein the short chain diol is selected from the group consisting of 1,4-butanediol (BDO) and 1,6-hexanediol (HDO), 1,3-propanediol (PDO) or mixtures thereof.

[0019] 8. The thermoplastic polyurethane composition according to any one of embodiments 1 to 7, wherein the chain extender component comprises or consists of 1,4-butanediol.

[0020] 9. The thermoplastic polyurethane composition according to any one of embodiments 1 to 7, wherein the chain extender component comprises or consists of 1,3-propanediol (PDO), optionally wherein the diisocyanate component is selected from the group consisting of aromatic diisocyanates and aliphatic diisocyanates or mixtures thereof.

[0021] 10. The thermoplastic polyurethane composition of any one of embodiments 1 to 9, wherein the diisocyanate component is selected from diphenyl diisocyanate (MDI), hexamethylene diisocyanate (HDI), or mixtures thereof.

[0022]

[0023] 11. The thermoplastic polyurethane composition of any one of embodiments 1 to 10, wherein the diisocyanate component comprises or consists of MDI.

[0024] 12. The thermoplastic polyurethane composition of any one of embodiments 1 to 11, wherein the diisocyanate component comprises or consists of HDI.

[0025] 13. The thermoplastic polyurethane composition according to any one of embodiments 1 to 12, wherein the thermoplastic polyurethane has a hard segment content of 2 to 50 wt. % or 7 to 36 wt%.

[0026] 14. The thermoplastic polyurethane composition according to any one of embodiments 1 to 13, wherein the thermoplastic polyurethane shows a shore D hardness of at least 60, or at least 70, or at least 80, or at least 86, or at least 90 as determined by ISO 7619-1:2010.

[0027] 15. The thermoplastic polyurethane composition according to any one of embodiments 1 to 14, wherein the thermoplastic polyurethane shows a recovery stress of from 1 to 30 MPa, preferably from 14 to 30 MPa.

[0028] 16. The thermoplastic polyurethane composition according to any one of embodiments 1 to 15, wherein the thermoplastic polyurethane shows energy output of from 0.6 to 30 MJ/m³ or from 8 to 30 MJ/m³.

[0029] 17. A molded article comprising the thermoplastic polyurethane composition according to any one of embodiments 1 to 16.

[0030] 18. A molded article according to embodiment 17, wherein the molding article is a medical device.

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DETAILED DESCRIPTION OF THE INVENTION

[0031] The articles "a" and "an" are used herein to refer to one or to more than one (i.e., to at least one) of the grammatical object of the article unless the context clearly indicates otherwise. By way of example, "an element" means one element or more than one element.

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[0032] Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word "about". The term "about" as used herein, e.g. when referring to a measurable value (such as an amount or weight of a particular component or temperature), refers to variations of $\pm 20\%$, $\pm 10\%$, $\pm 5\%$, $\pm 1\%$, $\pm 0.5\%$, or, particularly, $\pm 0.1\%$ of the specified amount. Except where otherwise indicated, all numerical quantities in the description specifying amounts or ratios of materials are on a weight basis.

15

[0033] As used herein, the term "comprising", which is inclusive or open-ended and does not exclude additional unrecited elements or method steps, is intended to encompass as alternative embodiments, the phrases "consisting essentially of" and "consisting of" where "consisting of" excludes any element or step not specified and "consisting essentially of" permits the inclusion of additional unrecited elements or steps that do not materially affect the essential or basic and novel characteristics of the composition or method under consideration.

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[0034] Temperature activated shape memory polymers are materials that can switch between a permanent and preprogramed temporary shape depending on their temperature. Said materials can be deformed and cooled below their switching temperature to their temporary shape, which will be stored by the material until the temperature is increased again and overcomes the switching temperature.

30

[0035] The present invention provides shape memory TPU compositions with desirable hardness, recovery stress, energy output and temperature resilience.

Polyester polyol component

[0036] The polyester polyol comprises a short chain diol and 2,5-furandicarboxylic acid (FDCA).

[0037] FDCA is member of the class of furans carrying two carboxy substituents at positions 2 and 5. FDCA is a renewable carboxylic acid that can prepared from carbohydrates and is also found as a natural product, for example as a natural product found in fungi such as *Phomopsis velata*.

[0038] Suitable short-chain diols include for example those having from 2 to 12 carbon atoms. Suitable diols may include, for example, ethylene glycol, 1,2-propanediol, 1,3-propanediol (PDO), 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol (HDO), 2,2-dimethyl-1,3-propanediol, 1,4-cyclohexane dimethanol, decamethylene glycol, dodecamethylene glycol, and the like. Particularly, the short-chain diol used in the invention may be HDO, PDO or mixtures thereof. In one embodiment the short-chain diol comprises, or even consist essentially of HDO. In one embodiment the short-chain diol comprises, or even consist essentially of PDO.

[0039] In one embodiment, the number average molecular weight (M_n) of the polyol component of the present invention, which can comprise polyols as defined above, is from about 250 to about 5,000, for example, about 1,000 to about 3,000 Da. When referred to herein, the M_n of the polyols is determined by ^1H NMR end-group analysis, through the integration of the signals corresponding to the protons of the terminal CH_2OH and alpha ester protons.

[0040] In one embodiment, the molar ratio of 2,5-furandicarboxylic acid to short chain diol of the polyester polyol (a) is from 1:1 to 1:5 or 1:1 to 1:2, or 1:1 to 1:1.5, or 1:1 to 1:1.25

Diisocyanate component

[0041] The diisocyanate component of the present invention can be selected from any diisocyanate known to those skilled in the art. Useful diisocyanates can be selected from aromatic isocyanates, aliphatic isocyanates or combinations thereof. Non-limiting examples of useful diisocyanates can include aromatic diisocyanates such as 4,4'-methylenebis(phenyl isocyanate) (MDI), 3,3'-dimethyl-4,4'-biphenylene diisocyanate (TODI), m-xylene diisocyanate (XDI), 1,4-phenylene diisocyanate, 1,5-naphthalene diisocyanate (NDI), and toluene diisocyanate (TDI), as well as aliphatic diisocyanates such as isophorone diisocyanate (IPDI), 1,4-cyclohexyl diisocyanate (CHDI), 1,6-hexamethylene diisocyanate (HDI), 1,10-decamethylene diisocyanate, lysine diisocyanate (LDI), 1,4-butane diisocyanate (BDI), and 4,4'-dicyclohexylmethane

diisocyanate (H12MDI). Mixtures of two or more diisocyanates may be used. Particularly, the diisocyanate can be MDI and/or HDI. More particularly, the diisocyanate component comprises or even consists essentially of MDI. In some embodiments, the diisocyanate component comprises or even consists essentially of HDI.

5 **[0042]** The thermoplastic polyurethane composition can comprise the reaction product of a polyester polyol comprising a short chain diol selected from the group consisting of PDO and HDO, and 2,5-furandicarboxylic acid (FDCA); a diisocyanate component comprising or consisting essentially of MDI and/or HDI; and a chain extender.

10 **[0043]** In one embodiment, the thermoplastic polyurethane composition may comprise of the reaction product of a polyester polyol comprising PDO and 2,5-furandicarboxylic acid (FDCA); a diisocyanate component selected from the group consisting of MDI and HDI or mixtures thereof, and a chain extender.

15 **[0044]** In another embodiment, the thermoplastic polyurethane composition may comprise or consist of the reaction product of a polyester polyol comprising, consisting essentially of, or consisting of PDO and 2,5-furandicarboxylic acid (FDCA); a diisocyanate component comprising or consisting of MDI and a chain extender. In still another embodiment, the thermoplastic polyurethane composition may comprise or consist of the reaction product of a polyester polyol comprising, consisting essentially of, or consisting of PDO and 2,5-furandicarboxylic acid (FDCA); a diisocyanate component comprising or consisting of HDI and a chain extender.

20 **[0045]** In another embodiment, the thermoplastic polyurethane composition may comprise or consist of the reaction product of a polyester polyol comprising, consisting essentially of or consist of HDO and 2,5-furandicarboxylic acid (FDCA); a diisocyanate component comprising or consisting of HDI and a chain extender. In another embodiment, the thermoplastic polyurethane may comprise or consist of the reaction product of a polyester polyol comprising, consisting essentially of, or consisting of HDO and 2,5-furandicarboxylic acid (FDCA); a diisocyanate component comprising or consisting of MDI and a chain extender.

Chain Extenders

30 **[0046]** Chain extenders are desirably employed in the polyurethane formulations of the present invention to increase the molecular weight thereof. They are also responsible for formation of crystalline hard blocks leading to thermoplastic polyurethanes with desirable mechanical properties.

35 **[0047]** Suitable chain extenders include relatively small polyhydroxy compounds, for example, lower aliphatic or short chain diols having from 2 to 20, or 2 to 12, or 2 to 10

carbon atoms. Suitable examples include ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, dipropylene glycol, 1,4- butanediol (BDO), 1,6-hexamethylene diol (HDO), 1,3-butanediol, 1,5-pentanediol, neopentylglycol, 1,4-cyclohexanedimethanol (CHDM), 2, 2-bis[4-(2 -hydroxy ethoxy) phenyl]propane (HEPP), heptanediol, nonanediol, dodecanediol, 3 -methyl -1,5-pentanediol, ethylenediamine, butanediamine, hexamethylenediamine, and hydroxy ethyl resorcinol (HER), pentaspiro glycol (PSG), hydroquinone bis(2-hydroxy ethyl) ether hydroquinone (HQEE), dipropylene glycol (DPG), 2-methyl-1,3-propane diol, 2-butyl-2-ethyl-1,3-propane diol (BEPD), and the like, as well as mixtures thereof. In one embodiment, the chain extender comprises, or even consist essentially of 1,4-butanediol (BDO).

[0048] The molar ratio of chain extender to polyol can be from 1:1 to 1:9.

[0049] The hard segment content of a thermoplastic polyurethane composition is defined as the combined weight percent of the diisocyanate component and the chain extender component.

[0050] One of the advantages of the TPU compositions of the present invention is that they show high hardness even at low concentrations of hard segment.

[0051] Thus, in some embodiments of the present invention, the thermoplastic polyurethanes herein can have a hard segment content of 50% by weight or lower. Particularly, the hard segment content can be of 2% to 50% by weight, or from 7 to 36 % by weight.

[0052] In one embodiment, the thermoplastic polyurethane composition shows a shore D hardness of at least 60, or of at least 70, or of at least 80, or of at least 86 or of at least 90 as determined by ISO 7619-1:2010.

[0053] The thermoplastic polyurethane composition can have a shore D hardness as determined by ISO 7619-1:2010 of at least 61 and a hard segment content from 7 to 36 % by weight.

[0054] The thermoplastic polyurethane composition can have a molar ratio of chain extender to polyol from 1:1 to 1:9.

[0055] In one embodiment, the diisocyanate is in an amount to provide a NCO:OH molar ratio from 1:1.25 to 1.25:1, particularly from 1:1.1 to 1.1:1

[0056] In some embodiments, the TPU compositions of the present invention exhibit desirable elongation and strain properties. For example, the TPU compositions may have an ultimate tensile strength of at least of 28 MPa and strain of at least of 11%, when measured using a dumbbell sample prepared according to ISO 37 1A and using the process according to ISO 37 1A with the modification that a rate of 5 mm/min at 21°C is

used. TPU compositions may also be tested for shape fixity (R_f) and recovery (R_r) properties. Shape fixity refers to the percentage of the elongation induced into the material that is maintained at 20 °C below the transition temperature of the material under no load after it being deformed to its temporary shape and it is calculated as follows:

$$R_f = \frac{\varepsilon_f(n)}{\varepsilon_m} \times 100$$

Where $\varepsilon_f(n)$ is the strain of the system after elongation at 20 °C below the transition temperature once the stress has been released and ε_m is the maximum strain applied to the system. Shape recovery refers to the percentage of the initial shape before deformation that is recovered once the material is heated to 20 °C above the transition temperature of the material under no load after its deformation to the temporary shape and it is calculated as follows:

$$R_r = \frac{\varepsilon_f(n) - \varepsilon_r(n)}{\varepsilon_m - \varepsilon_0} \times 100$$

Where $\varepsilon_f(n)$ is the strain of the system after elongation at 20 °C below the transition temperature once the stress has been released, ε_m is the maximum strain applied to the system, $\varepsilon_r(n)$ is the strain of the sample in the stress-free state at 20 °C above the transition temperature after the 30 minutes of recovery time and ε_0 is the strain of the sample at the start of the cycle. Shape fixity and recovery may be measured by a process involving the following steps: (1) Set the temperature to 20 °C above the T_g of the materials; (2) Isothermal hold for 5 minutes; (3) Increase strain to 100% at a rate of 50%/min; (4) Isothermal hold for 5 minutes; (5) Decrease temperature to 20 °C below T_g at a rate of - 10 °C/min; (6) Isothermal hold for 5 minutes; (7) Set force to 0.001N; (8) Isothermal hold for 5 minutes; (9) Increase temperature to 20 °C above the T_g of the materials at a rate of 10 °C/min; (10) Isothermal for 30 minutes. Step 3-10 are repeated two times to complete three cycles to report results. The equipment for measuring shape fixity and recovery may be measured any known suitable instruments, such as a DMA Q800 from TA Instruments.

[0057] Desirable properties for shape memory polymers include good recovery stress and energy output. These two properties define how much strength (recovery stress) and energy output (volumetric energy density) the material is capable of generating when moving from the temporary shape to the permanent one. TPU compositions as disclosed herein have been observed to exhibit recovery stress and energy output.

[0058] The TPU compositions disclosed herein can have a recovery stress of from 1 to 30 MPa, particularly of from 14 to 30 MPa.

[0059] Based on the detailed examples the skilled person is routinely able to repeat the assay to objectively determine the recovery stress of the TPU compositions.

5 [0060] For example, to measure the recovery stress of the TPU compositions, the recovery stress is determined at 20°C above the glass transition temperature (T_g) of each material on ISO37 1A dumbbell samples. The value corresponds to the stress of the material once it has been elongated to 90% of its ultimate strain at 20°C above the T_g and then allowed to relax with fixed elongation for 5 minutes. The T_g of samples can be
10 measured using the method following ISO 11357-2. As used in the present invention, T_g was measured using IS 11357-2, but employing a heating and cooling rate of 10 °C/min.

[0061] The TPU compositions disclosed herein can have an energy output (volumetric energy density) of from 0.6 to 30 MJ/m³, particularly from 8 to 30 MJ/m³, more particularly from 20 to 30 MJ/m³.

15 [0062] Based on the detailed examples the skilled person is routinely able to repeat the assay to objectively determine the energy output of the TPU compositions.

[0063] For example, in order to measure the energy output (volumetric energy density) of the TPU compositions, the energy output is calculated as the extrapolated area between the Recovery Stress and its elongation as reported in Copper et al.
20 [Cooper, C et al. High Energy Density Shape Memory Polymers Using Strain-Induced Supramolecular Nanostructures. *ACS Cent. Sci.* **2021**, 7 (10), 1657–1667. <https://doi.org/10.1021/acscentsci.1c00829>] as follows:

$$\text{Energy output} = \frac{0.5 \times \text{Recovery Stress} \times \text{Elongation at Recovery Stress (\%)}}{100}$$

25 [0064] TPU compositions of the present invention are formed by reacting a polyester polyol component and a hard segment component comprising a diisocyanate and a chain extender, and optionally, a catalyst.

30 [0065] The three reactants (the polyol polyester, the diisocyanate, and the chain extender) are reacted together to form the TPU of this invention. Any known processes to react the three reactants may be used to make the TPU.

[0066] The process can be the so-called “one-shot” process where all three reactants are added to an extruder reactor and reacted. The reaction may comprise

melting the polyol at 140 to 180 °C and adding diisocyanates and chain extender, and optionally catalyst and/or additives.

[0067] Thus, in one embodiment, the process comprises melting the polyester polyol at a temperature from 140 to 180 °C to melt the polyester polyol and adding the diisocyanate and chain extender. The process may further include adding catalysts and/or additives.

[0068] The TPU can also be prepared utilizing a pre-polymer process. In the pre-polymer route, the polyol intermediates are generally reacted with an equivalent excess of one or more diisocyanates to form a pre-polymer solution having free or unreacted diisocyanate therein. The reaction is generally carried out at temperatures of from about 80 to about 220 °C, or from about 150 to about 200 °C, optionally, in the presence of a suitable urethane catalyst. Subsequently, a chain extender, as noted above, is added in an equivalent amount generally equal to the isocyanate end groups as well as to any free or unreacted diisocyanate compounds. The chain extension reaction temperature is generally from about 180 to about 250 °C or from about 200 to about 240 °C. Typically, the pre-polymer route can be carried out in any conventional device including an extruder. In such embodiments, the polyol intermediates are reacted with an equivalent excess of a diisocyanate in a first portion of the extruder to form a pre-polymer solution and subsequently the chain extender is added at a downstream portion and reacted with the pre-polymer solution. Any conventional extruder can be utilized, including extruders equipped with barrier screws having a length to diameter ratio of at least 20 and in some embodiments at least 25.

Auxiliary substances and catalysts

[0069] Optionally, catalysts, auxiliary substances and/or additives can be used in the polyurethane reaction mixtures of the present invention.

[0070] Any of the catalysts conventionally employed or known in the art to catalyze the reaction of an isocyanate with a reactive hydrogen containing compound can be employed for this purpose. Examples of suitable catalysts which in particular accelerate the reaction between the NCO groups of the diisocyanates and the hydroxy groups of the polyols and chain extenders are the conventional tertiary amines known from the prior art, e.g. triethylamine, dimethyl cyclohexylamine, N-methylmorpholine, N,N'-dimethylpiperazine, 2-(dimethylaminoethoxy)ethanol, diazabicyclo[2,2,2]octane and the like, and also in particular organometallic compounds, such as titanate esters, iron compounds, e.g. ferric acetyl acetonate, bismuth compounds, e.g. bismuth octanoate,

bismuth neodecanoate, bismuth laureate, tin compounds, e.g. stannous diacetate, stannous dioctoate, stannous dilaurate, or the dialkyltin salts of aliphatic carboxylic acids, e.g. dibutyltin diacetate, dibutyltin dilaurate, or the like phenyl mercuric propionate, lead octoate, iron acetylacetonate, magnesium acetylacetonate, and the like. Mixtures of the above noted catalysts can likewise be used.

[0071] Auxiliary substances and/or additives may also be added. Suitable, non-limiting examples include lubricants such as fatty acid esters, their metal soaps, fatty acid amides, fatty ester amides and silicone compounds, anti-blocking agents, inhibitors, stabilizers against hydrolysis, light, heat and discoloration, flameproofing agents, flame retardant agents, dyes, pigments, inorganic and/or organic fillers and reinforcing agents.

Applications

[0072] Thermoplastic polyurethane (TPU) compositions described above are highly useful materials that can provide an attractive combination of physical properties, particularly mechanical and shape memory properties.

[0073] The compositions of the invention and any blends thereof are useful in a wide variety of applications. Non-limiting examples of articles comprising the TPU compositions of the invention may include cook and storage ware, articles such as furniture, automotive components, toys, sportswear, medical devices, eyeglasses, including eyeglass frames and temple pieces, sterilizable medical devices, sterilization containers, fibers, woven fabrics, nonwoven fabrics, drapes, gowns, filters, hygiene products, diapers, and films, oriented films, sheets, tubes, pipes, wire jacketing, cable jacketing, agricultural films, geomembranes, sporting equipment, cast film, blown film, boat and water craft components, and other such articles. The compositions may be suitable for automotive components such as bumpers, grills, trim parts, dashboards and instrument panels, exterior door and hood components, spoiler, wind screen, windshield wipers, hub caps, mirror housing, body panel, protective side molding, and other interior and external components associated with automobiles, trucks, boats, and other vehicles.

[0074] Other useful articles may be formed from the compositions of the invention including: crates, containers, packaging, labware, such as roller bottles for culture growth and media bottles, office floor mats, instrumentation sample holders and sample windows; liquid storage containers such as bags, pouches, and bottles for storage and IV infusion of blood or solutions; packaging material including those for any medical device or drugs including unit-dose or other blister or bubble pack as well as for wrapping or containing food preserved by irradiation. Other useful items include medical tubing and valves for any medical device including infusion kits, catheters, and respiratory

therapy, as well as packaging materials for medical devices or food which is irradiated including trays, as well as stored liquid, particularly water, milk, or juice, containers including unit servings and bulk storage containers as well as transfer means such as tubing, hoses, pipes, and such, including liners and/or jackets thereof.

5 [0075] In the medical field, suture threads that have their shape memory switch temperature at around body temperature can be generated. These sutures, upon reaching body temperature would tighten, securing the stiches without requiring the intervention of the surgeon. Self-expanding shape memory stents allow the deployment of contracted stents that, upon being placed in position and heated by the body
10 temperature, expand to their full size. This allows an easier insertion of the stent and minimizes the harm done upon introduction of the device.

[0076] Light weight self-deployable structures for smart buildings, like in adaptive sun shading, or for the aerospace field, like solar sails can also be made.

[0077] The articles can be made or prepared by any useful process for forming
15 thermoplastic polyurethane materials. This will include, at least, molding, including compression molding, injection molding, blow molding, and transfer molding; film blowing or casting; extrusion, and thermoforming; as well as by lamination, pultrusion, draw reduction, rotational molding, spin-bonding, melt spinning, melt blowing; fiber spinning, electrospinning or combinations thereof. Use of at least thermoforming or film
20 applications allows for the possibility of and derivation of benefits from uniaxial or biaxial orientation of the material.

[0078] The present invention will be better understood by reference to the following examples, which serve to illustrate the invention, but not to limit the same.

25 EXAMPLES

Abbreviations

The following abbreviations are used in the examples: MDI= 4,4'-methylenebis(phenyl isocyanate) and HDI=1,6-hexamethylene diisocyanate.

30 Synthesis of thermoplastic polyurethanes

A series of different thermoplastic polyurethanes were synthesised as disclosed in Table 1 using 1,4-butanediol as chain extender. The NCO:OH ratio was of 1:1. The shore D hardness and glass transition temperature (T_g) of the materials of the Examples were determined according to the following methods:

- 35 - Hardness was calculated according to ISO 7619-1:2010

- Glass transition temperature was determined on DSC as the mean of the T_g values of the second cooling and heating. Data obtained using a heating/cooling rate of 10 °C/min.

The measured hardness and T_g values are included in Table 1.

5 Table 1: TPU Compositions and Physical Properties

Ex.	Polyester	Polyester M_n (g/mol)	Diisocyanate	Hard Segment (wt%)	Hardness (Shore D)	T_g (°C)
1	Polypropylene isophthalate	990	MDI	22.6	81	60.2
2	Polypropylene isophthalate	1090	MDI	26.7	81	58.9
3	Polypropylene isophthalate	1110	MDI	34.7	77	65.1
4	Polypropylene isophthalate	1950	MDI	12.9	81	48.6
5	Polypropylene isophthalate	1950	MDI	16.9	86	51.9
6	Polypropylene isophthalate	2300	MDI	20.4	80	58.7
7	Polyhexamethylene isophthalate	1030	MDI	21.9	70	28.7
8	Polyhexamethylene isophthalate	1030	MDI	27.8	74	36.3
9	Polyhexamethylene isophthalate	1030	MDI	36.5	75	42.2
10	Polyhexamethylene isophthalate	1910	MDI	13.1	33	19.0
11	Polyhexamethylene isophthalate	1930	MDI	17.0	39	23.5
12	Polyhexamethylene isophthalate	2020	MDI	22.6	65	26.8
13	Polypropylene isophthalate	1110	HDI	15.1	81	30.6
14	Polypropylene isophthalate	1130	HDI	19.8	81	28.9
15	Polypropylene isophthalate	1110	HDI	27.8	72	26.9
16	Polypropylene isophthalate	2380	HDI	7.7	75	34.1
17	Polypropylene isophthalate	2480	HDI	10.1	74	32.7
18	Polypropylene isophthalate	2520	HDI	14.5	72	31.6
19	Polyhexamethylene isophthalate	1180	HDI	14.3	32	2.9
20	Polyhexamethylene isophthalate	1180	HDI	19.1	36	5.3

21	Polyhexamethylene isophthalate	1180	HDI	26.5	45	5.2
22	Polyhexamethylene isophthalate	1900	HDI	9.4	33	4.8
23	Polyhexamethylene isophthalate	1680	HDI	14.2	39	5.2
24	Polyhexamethylene isophthalate	1920	HDI	18.2	39	6.5
25	Polypropylene 2,5-furandicarboxylate	1130	MDI	20.4	90	68.7
26	Polypropylene 2,5-furandicarboxylate	1060	MDI	35.9	91	65.8
27	Polypropylene 2,5-furandicarboxylate	1660	MDI	19.2	96	60.4
28	Polypropylene 2,5-furandicarboxylate	1820	MDI	13.7	95	55.5
29	Polypropylene 2,5-furandicarboxylate	2210	MDI	21.1	96	60.7
30	Polyhexamethylene 2,5-furandicarboxylate	1200	MDI	19.4	96	12.2
31	Polyhexamethylene 2,5-furandicarboxylate	1220	MDI	32.6	94	44.1
32	Polyhexamethylene 2,5-furandicarboxylate	1620	MDI	19.7	96	30.9
33	Polyhexamethylene 2,5-furandicarboxylate	2110	MDI	12.0	95	26.6
34	Polyhexamethylene 2,5-furandicarboxylate	2130	MDI	21.7	96	30.2
35	Polypropylene 2,5-furandicarboxylate	1050	HDI	16.1	93	40.8
36	Polypropylene 2,5-furandicarboxylate	1040	HDI	30.4	93	36.6
37	Polypropylene 2,5-furandicarboxylate	1560	HDI	15.7	94	43.6
38	Polypropylene 2,5-furandicarboxylate	2010	HDI	9.1	95	47.7
39	Polypropylene 2,5-furandicarboxylate	1990	HDI	18.6	93	42.9
40	Polyhexamethylene 2,5-furandicarboxylate	1180	HDI	14.4	61	9.6
41	Polyhexamethylene 2,5-furandicarboxylate	1050	HDI	28.8	62	11.5
42	Polyhexamethylene 2,5-furandicarboxylate	1660	HDI	14.4	65	11.9
43	Polyhexamethylene 2,5-furandicarboxylate	1820	HDI	9.8	66	13.6
44	Polyhexamethylene 2,5-furandicarboxylate	1950	HDI	17.9	63	12.2
45	Polybutylene adipate	1000	MDI	50.0	33	n.d.
46	Polybutylene adipate	1000	MDI	88.2	60	n.d.

As general trend, the hardness of TPUs with similar hard segment content is higher for FDCA than standard TPUs with aliphatic polyols (*i.e.* ADPBDO) and even higher than TPUs made with other aromatic polyols, such as IPHTA. The same trend was observed for glass transition temperature.

5 Recovery Stress/Energy Output/Resilience Measurements

[0079] For each of the Example TPU compositions, recovery stress, energy output, and resilience temperature were measured.

[0080] Recovery stress and energy output were measured as described herein using a DMA Q800 from TA Instruments at 20°C above the T_g of each material on ISO37 1A dumbbell samples. To determine the recovery stress of the sample, the material was elongated to 90% of its maximum strain at a rate of 50%/minute. Then, the material was allowed to relax under fixed elongation during 5 minutes and the value of stress posterior to said relaxation was selected as the recovery stress of the material.

[0081] Energy output (volumetric energy density) was calculated as the extrapolated area between the Recovery Stress and its elongation as reported in Copper et al. [Cooper, C et al.. High Energy Density Shape Memory Polymers Using Strain-Induced Supramolecular Nanostructures. *ACS Cent. Sci.* **2021**, 7 (10), 1657–1667. <https://doi.org/10.1021/acscentsci.1c00829>] as follows:

20
$$\text{Energy output} = \frac{0.5 \times \text{Recovery Stress} \times \text{Elongation at Recovery Stress (\%)}}{100}$$

[0082] The resilience to temperature of the mechanical properties of the TPU compositions has been studied by dynamic mechanical analysis. This resilience is important as, the higher it is, the higher the maximum service temperature of the materials will be. Therefore, if the materials are to be used for applications in which the material is required to withstand high temperatures, high resilience to temperature is needed. For assessing the trends of these temperature resilience, dynamic mechanical analysis (DMA) has been employed. This has been done by using the ASTM D4045-06 test with the modification that the material is heated at a rate of 5°C/minute from -50°C at a frequency of 1Hz with a 10 μm amplitude on a dual cantilever clamp on 35x15x2.5-3mm samples and determining the temperature at which the material reached a storage modulus of 5MPa.

[0083] The results of the Recovery Stress, Energy Output, and Resilience measurements are listed in Table 2.

Table 3: Energy output and recovery stress of each of the samples

Ex.	Recovery Stress (MPa)	Energy output (MJ/m ³)	Resilience Temperature (°C)
1	<0.5	<0.3	118
2	1.2	2.0	116
3	<0.5	<0.3	145
4	<0.5	<0.3	124
5	0.7	0.6	119
6	0.7	0.7	110
7	0.9	2.0	90
8	1.0	1.5	102
9	1.8	2.1	105
10	2.3	0.5	87
11	2.6	5.5	91
12	1.9	3.6	115
13	1.3	2.6	89
14	1.0	0.8	80
15	4.2	5.0	108
16	1.1	2.1	95
17	1.1	1.4	93
18	1.8	1.1	116
19	7.2	11.3	70
20	15.5	21.6	83
21	10.9	7.4	112
22	13.0	16.3	80
23	9.2	7.0	88
24	12.3	10.0	120
25	1.1	0.9	193
26	3.1	1.4	166
27	1.0	0.3	127
28	2.7	0.8	183
29	1.2	0.3	185
30	3.5	3.4	127
31	1.2	1.2	110
32	3.9	3.1	126
33	10.9	8.8	110
34	7.1	6.5	130
35	2.2	0.8	196
36	4.3	1.8	188
37	4.4	6.1	192
38	5.5	6.9	170
39	7.1	6.7	190
40	15.3	9.1	178
41	14.8	8.0	162
42	25.6	24.7	181
43	24.0	21.0	188
44	26.3	25.4	143

[0084] For TPUs with similar composition the recovery stress and energy output were higher for those polymers comprising FDCA. Moreover, the resilience to temperature of the FDCA TPUs was higher than for the IPHTA ones.

- 5 **[0085]** The invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

CLAIMS:

1. A thermoplastic polyurethane composition comprising the reaction product of:
 - (a) a polyester polyol comprising a short chain diol and 2,5-furandicarboxylic acid;
 - (b) a diisocyanate component; and
 - (c) a chain extender component.
2. The thermoplastic polyurethane composition according to claim 1, wherein the polyester polyol has a number average molecular weight lower than 5,000 Da.
3. The thermoplastic polyurethane composition according to either claim 1 or claim 2, wherein the polyester polyol has a number average molecular weight in the range from 800 to 5,000 Da, preferably from 1,000 to 3,000 Da.
4. The thermoplastic polyurethane composition according to any one of claims 1 to 3, wherein the diisocyanate is in an amount to provide a NCO:OH molar ratio of from 1:1.25 to 1.25:1.
5. The thermoplastic polyurethane composition according to any one of claims 1 to 4, wherein the molar ratio of chain extender to polyol is from 1:1 to 1:9.
6. The thermoplastic polyurethane composition according to any one of claims 1 to 5, wherein the molar ratio of 2,5-furandicarboxylic acid to short chain diol of the polyester polyol (a) is from 1:1 to 1:5 or 1:1 to 1:2, or 1:1 to 1:1.5, or 1:1 to 1:1.25.
7. The thermoplastic polyurethane composition according to any one of claims 1 to 6, wherein the short chain diol is selected from the group consisting of 1,4-butanediol (BDO) and 1,6-hexanediol (HDO), 1,3-propanediol (PDO) or mixtures thereof.
8. The thermoplastic polyurethane composition according to any one of claims 1 to 7, wherein the chain extender component comprises or consists of 1,4-butanediol.
9. The thermoplastic polyurethane composition according to any one of claims 1 to 7, wherein the chain extender component comprises or consists of 1,3-propanediol (PDO).
10. The thermoplastic polyurethane composition of any one of claims 1 to 9, wherein the diisocyanate component is selected from diphenyl diisocyanate (MDI), hexamethylene diisocyanate (HDI), or mixtures thereof.
11. The thermoplastic polyurethane composition of any one of claims 1 to 10, wherein the diisocyanate component comprises or consists of MDI.
12. The thermoplastic polyurethane composition of any one of claims 1 to 11, wherein the diisocyanate component comprises or consists of HDI.

13. The thermoplastic polyurethane composition according to any one of claims 1 to 12, wherein the thermoplastic polyurethane has a hard segment content of 2 to 50 wt. % or 7 to 36 wt%.
14. The thermoplastic polyurethane composition according to any one of claims 1 to 13, wherein the thermoplastic polyurethane shows a shore D hardness of at least 60, or at least 70, or at least 80, or at least 86, or at least 90 as determined by ISO 7619-1:2010.
15. The thermoplastic polyurethane composition according to any one of claims 1 to 14, wherein the thermoplastic polyurethane shows a recovery stress of from 1 to 30 MPa, preferably from 14 to 30 MPa.
16. The thermoplastic polyurethane composition according to any one of claims 1 to 15, wherein the thermoplastic polyurethane shows energy output of from 0.6 to 30 MJ/m³ or from 8 to 30 MJ/m³.
17. A molded article comprising the thermoplastic polyurethane composition according to any one of claims 1 to 16.
18. A molded article according to claim 17, wherein the molding article is a medical device.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2023/032681

A. CLASSIFICATION OF SUBJECT MATTER INV. C08G18/32 C08G18/42 C08G18/66 C08G18/73 C08G18/76 ADD.		
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) C08G		
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) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 3 105 270 A1 (CRODA INT PLC [GB]) 21 December 2016 (2016-12-21)	1-4, 6-16
Y	paragraphs [0001], [0008], [0057] - [0063], [0077], [0127]; claims; examples P1, E5	5, 12, 17, 18
Y	DE 10 2020 001754 A1 (FRAUNHOFER GES FORSCHUNG [DE]) 23 September 2021 (2021-09-23) paragraphs [0001], [0006], [0017], [0019], [0038] - [0040]; claims; examples	5, 12, 17, 18
A	EP 0 364 869 A2 (MITSUBISHI HEAVY IND LTD [JP]) 25 April 1990 (1990-04-25) column 1, lines 4-7 column 4, lines 19-41; claims; examples 18-20; table 1	1-17
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☒ 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 but 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 1 December 2023		Date of mailing of the international search report 14/12/2023
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Eigner, Markus

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2023/032681

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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