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THERMOPLASTIC POLYURETHANE COMPOSITIONS

FIELD OF THE INVENTION

5 [0001] The present invention relates to thermoplastic polyurethane (TPU) compositions with excellent biostability and superior resistance to environmental stress cracking. Such combination of properties makes the TPU compositions described herein useful materials for medical applications.

BACKGROUND OF THE INVENTION

10 [0002] Thermoplastic polyurethanes (TPUs) are polymeric materials extensively used in the fabrication of medical devices. The physical properties of polyurethanes can typically be adjusted for various applications through the selection of the type and number of starting materials (for example polyol, isocyanate, and chain extender) used in the composition to obtain polymers with properties particularly suitable for in vivo applications. The chemical, physical and thermomechanical properties depend upon the specific function, the type of tissue, cells or fluids contacting the medical device and the acceptable or desired manufacturing processes. Common considerations when choosing polymers for medical devices are based on parameters such as stiffness, flexibility, chemical stability of the polymer, particularly hydrolytic stability, the toxicity of the polymer, and the degree of interaction between tissue or blood and the polymer. Particularly, 15 biostability is of major importance for implant applications.

20 [0003] WO2016054320A1, for example, discloses TPU compositions having non-softening and wet flexibility suitable for medical devices. However, their use in long term implants may be compromised due to its susceptibility to oxidative attack and/or biostability.

25 [0004] One limitation of TPUs is that they can undergo numerous changes when exposed to a chemical environment. Environmental stress cracking (ESC) can occur when a polymer is placed under tensile stress in the presence of an active chemical agent. The potential for environmental stress cracking is of paramount concern in medical devices. In medical applications, chemicals such as isopropanol can initiate crazes - microcracks bridged by polymer fibrils- in the material and seriously compromise its 30 mechanical integrity. Cracking and embrittlement are a sign of an inherent weakness in

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the material which could result in unpredictable material failures. Furthermore, alcohols are common solvents used in the manufacturing processes and assembly of medical devices as well as a common cleaning agent in the hospital setting.

5 **[0005]** Thus, there is still the need for TPUs that in addition to other physical properties necessary for their use as medical devices, have appropriate biostability and a desirable resistance to environmental stress cracking.

[0006] 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

10 **[0007]** The disclosed technology provides thermoplastic polyurethane (TPU) compositions with excellent biocompatibility and superior resistance to environmental stress cracking. The TPU compositions show also improved processability and suitable mechanical properties.

15 **[0008]** The invention provides a thermoplastic polyurethane composition comprising the reaction product of at least:

 a) a polyisocyanate comprising at least 50 wt.% based on the total weight of the polyisocyanate component of (i) an aliphatic diisocyanate having from 6 to 10 carbon atoms;

20 b) a polyol comprising at least a hydroxyl-terminated poly(butadiene) (HTPB); and,

 c) a chain extender comprising at least one diol chain extender of the general formula $\text{HO}-(\text{CH}_2)_x-\text{OH}$ wherein x is an integer from 2 to 6;

wherein the thermoplastic polyurethane composition has a hard segment of from 22 to 65 wt.% based on the total weight of the composition, wherein the hard segment content is defined as the combined weight of the polyisocyanate component a) and the chain extender component c). In particular, the amount of hard segment can be from 25 to 65 wt.%, or from 30 to 65 wt.%. More particularly, the amount of hard segment can be from 45 to 65 wt.%.
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30 **[0009]** The invention also relates to an article comprising the TPU compositions disclosed herein.

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[0010] The invention further provides a process of making the TPU compositions disclosed herein, said process comprising the step of reacting:

- a) a polyisocyanate comprising at least 50 wt.% based on the total weight of the polyisocyanate component of (i) an aliphatic diisocyanate having from 6 to 10 carbon atoms;
- b) a polyol comprising at least a hydroxyl-terminated poly(butadiene) (HTPB); and,
- c) a chain extender comprising at least one diol chain extender of the general formula $\text{HO}-(\text{CH}_2)_x\text{-OH}$ wherein x is an integer from 2 to 6;

wherein the amount of hard segment of the composition is from 22 to 65 wt.% based on the total weight of the composition. In particular, the amount of hard segment can be from 25 to 65 wt.%, or from 30 to 65 wt.%. More particularly, the amount of hard segment can be from 45 to 65 wt.%.

DETAILED DESCRIPTION OF THE INVENTION

[0011] Various preferred features and embodiments will be described below by way of non-limiting illustration.

[0012] 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.

[0013] 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.

[0014] 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

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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.

[0015] The disclosed technology provides a thermoplastic polyurethane composition comprising the reaction product of at least:

- a) a polyisocyanate comprising at least 50 wt.% based on the total weight of the polyisocyanate component of (i) an aliphatic diisocyanate having from 6 to 10 carbon atoms;
 - b) a polyol comprising at least a hydroxyl-terminated poly(butadiene) (HTPB); and,
 - c) a chain extender comprising at least one diol chain extender of the general formula $\text{HO}-(\text{CH}_2)_x-\text{OH}$ wherein x is an integer from 2 to about 6;
- wherein the thermoplastic polyurethane composition has a hard segment of from 22 to 65 wt.% based on the total weight of the composition, wherein the hard segment content is defined as the combined weight of the polyisocyanate component a) and the chain extender component c).

The polyisocyanate component

[0016] The TPU compositions described herein are made using (a) a polyisocyanate component, which includes at least 50 wt.% based on the total weight of the polyisocyanate component of (i) an aliphatic diisocyanate having from 6 to 10 carbon atoms.

[0017] Suitable aliphatic diisocyanates include linear and branched isocyanates, and cycloaliphatic diisocyanates (i.e., cyclic aliphatic diisocyanates).

[0018] In particular, the aliphatic diisocyanate (i) can be selected from the group consisting of 1,4-diisocyanatobutane (BDI), 1,5-diisocyanatopentane (PDI), hexamethylene diisocyanate (HDI), 1,8-diisocyanatooctane, 1,5-diisocyanato-2-methylpentane, 1,5-diisocyanato-2,2-dimethylpentane, 1,3-diisocyanatocyclohexane, 1,4-diisocyanatocyclohexane, 1,3-diisocyanato-2-methylcyclohexane, 1,3-diisocyanato-4-methylcyclohexane, 1,3-bis(isocyanatomethyl)cyclohexane (HXDI), 1,4-bis(isocyanatomethyl)cyclohexane (1,4-H6XDI) and mixtures thereof.

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[0019] The aliphatic diisocyanate (i) can be a linear aliphatic diisocyanate, more particularly hexamethylene diisocyanate (HDI).

[0020] The aliphatic diisocyanate (i) can be a cyclic aliphatic diisocyanate, particularly, 1,3-bis(isocyanatomethyl)cyclohexane (HXDI) or 1,4-bis(isocyanatomethyl)cyclohexane (1,4-H6XDI). More particularly, the aliphatic diisocyanate (i) can be 1,4-bis(isocyanatomethyl)cyclohexane (1,4-H6XDI).

[0021] The polyisocyanate (a) further comprises (ii) a cyclic aliphatic isocyanate different from the aliphatic diisocyanate (a)(i).

[0022] The cyclic aliphatic isocyanate (a)(ii) can have 6 to 12 carbon atoms. In particular, the cyclic aliphatic isocyanate (a)(ii) is 4,4'-diisocyanato dicyclohexylmethane (H12MDI).

[0023] In some embodiments, the polyisocyanate component is substantially free of, or even completely free of, aromatic diisocyanates.

[0024] In particular, the concentration of aliphatic diisocyanate (a)(i) can be from 55 to 75 wt.% based on the total weight of the polyisocyanate component, more particularly from 60 to 65 wt.%.

[0025] In some embodiments, the polyisocyanate component (a) essentially consist of, or even consist of (i) an aliphatic diisocyanate having from 6 to 10 carbon atoms and (ii) a cyclic aliphatic diisocyanate different from the aliphatic diisocyanate (i).

[0026] The polyisocyanate component (a) may comprise hexamethylene diisocyanate (HDI) and 4,4'-diisocyanato dicyclohexylmethane (H12MDI).

[0027] The polyisocyanate component (a) may comprise 1,4-bis(isocyanatomethyl)cyclohexane (1,4-H6XDI) and 4,4'-diisocyanato dicyclohexylmethane (H12MDI).

[0028] In some embodiments, the weight ratio from aliphatic diisocyanate (a)(i) to cyclic aliphatic isocyanate (a)(ii) is from 1:1 to 3:1. Particularly, the weight ratio can be from 1:1 to 2:1, more particularly from 1:1 to 1.5:1, still more particularly from 1.2:1 to 1.5:1.

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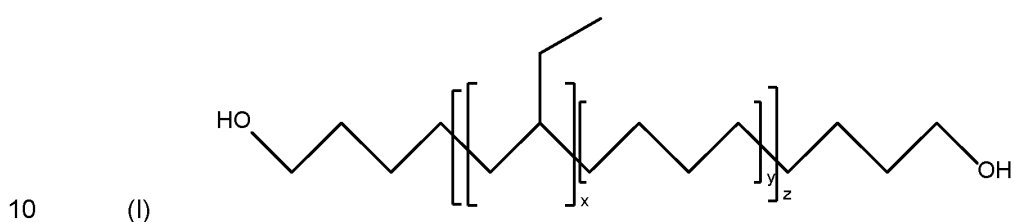
The polyol component

[0029] The TPU compositions described herein are made using (b) a polyol component comprising at least a hydroxy-terminated poly(butadiene) (HTPB).

5 [0030] The term 'hydroxy-terminated poly(butadiene)' (HTPB) refers to linear polybutadiene polymer with primary hydroxyl end groups.

[0031] The hydroxyl-terminated poly(butadiene) may be a hydroxyl-terminated hydrogenated polybutadiene.

[0032] In particular, the hydroxyl-terminated hydrogenated polybutadiene may be a compound selected from Formula (I):



wherein X is an integer from 10 to 20, Y is an integer from 1 to 10, and Z is an integer from 10 to 60.

15 [0033] The hydroxyl-terminated hydrogenated polybutadiene can be the compound of Formula (I), wherein Z is an integer from 20 to 40.

[0034] The hydroxyl-terminated hydrogenated polybutadiene can be the compound of Formula (I), wherein X is an integer from 10 to 15, Y can be from 5 to 10 and Z can be from 35 to 45. Particularly, X is 13, Y is 7 and Z is 40. Suitable, non-limiting examples, useful in the context of the invention is the hydrogenated hydroxyl-terminated polyol commercialized under the tradename Krasol® HLBH-P2000 by Cray Valley.

20 [0035] The hydroxyl-terminated hydrogenated poly(butadiene) can be the compound of Formula (I), wherein X is from 15 to 20, Y is from 1 to 5 and Z is from 15 to 25. Particularly, X can be 17, Y can be 3 and Z can be 20. A suitable, non-limiting example, useful in the context of the invention is a both-end hydroxyl group-terminated polybutadiene commercialized under the tradename Nisso™ GI-1000 by Nippon Soda Co., LTD.

25 [0036] In some embodiments, the polyol component can further comprise other optional polyols. Suitable polyols which may be used in combination with hydroxy-

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terminated poly(butadiene) polyol described above can include polyether polyols, polycarbonate polyols, polysiloxane polyols, polyester polyols including polycaprolactone polyester polyols, polyamide oligomers or any combinations thereof.

[0037] In other embodiments, the polyol component used to prepare the TPU composition of the present invention is free of one or more of these additional polyols, and in some embodiments the polyol component consists essentially of the hydroxy-terminated poly(butadiene) polyols described above. In a particular embodiment, the polyol component consists of hydroxy-terminated poly(butadiene), more particularly consist of hydroxyl-terminated hydrogenated polybutadiene.

[0038] Suitable polyether polyols may also be referred to as hydroxyl terminated polyether intermediates and include polyether polyols derived from a diol or polyol having a total of from 2 to 15 carbon atoms. In some embodiments, the diol or polyol is reacted with an ether comprising an alkylene oxide having from 2 to 6 carbon atoms, typically ethylene oxide or propylene oxide or mixtures thereof. For example, hydroxyl functional polyether can be produced by first reacting propylene glycol with propylene oxide followed by subsequent reaction with ethylene oxide. Primary hydroxyl groups resulting from ethylene oxide are more reactive than secondary hydroxyl groups and thus are preferred. Useful commercial polyether polyols include poly(ethylene glycol) (PEG) comprising ethylene oxide reacted with ethylene glycol, poly(propylene glycol) comprising propylene oxide reacted with propylene glycol, poly(tetramethylene glycol) comprising water reacted with tetrahydrofuran (PTMEG). In some embodiments, the polyether intermediate includes PTMEG or PEG or combinations thereof. Suitable polyether polyols also include polyamide adducts of an alkylene oxide and can include, for example, ethylenediamine adduct comprising the reaction product of ethylenediamine and propylene oxide, diethylenetriamine adduct comprising the reaction product of diethylenetriamine with propylene oxide, and similar polyamide type polyether polyols. Copolyethers can also be utilized in the technology described herein. Typical copolyethers include the reaction product of THF and ethylene oxide or THF and propylene oxide. These are available from BASF as Poly-THF®- B, a block copolymer, and poly-THF®- R, a random copolymer. The various polyether intermediates generally have a number average molecular weight (Mn) as determined by assay of the terminal functional groups which is an average molecular weight greater than about 700, or even from 700, 1,000, 1,500 or even 2,000

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up to 10,000, 5,000, 3,000, 2,500, 2,000 or even 1,000. In some embodiments, the polyether intermediate includes a blend of two or more different molecular weight polyethers, such as a blend of 2,000 Mn PTMO and 1,000 Mn PTMO.

[0039] Suitable polycarbonates may also be referred as hydroxyl terminated polycarbonates and include those prepared by reacting a glycol with a carbonate. U.S. Patent No. 4,131,731 is hereby incorporated by reference for its disclosure of hydroxyl terminated polycarbonates and their preparation. Such polycarbonates are linear and have terminal hydroxyl groups with essential exclusion of other terminal groups. The essential reactants are glycols and carbonates. Suitable glycols are selected from cycloaliphatic and aliphatic diols containing 4 to 40, and or even 4 to 12 carbon atoms, and from polyoxyalkylene glycols containing 2 to 20 alkoxy groups per molecular with each alkoxy group containing 2 to 4 carbon atoms. Suitable diols include aliphatic diols containing 4 to 12 carbon atoms such as 1,4-butanediol, 1,5-pentanediol, neopentyl glycol, 1,6-hexanediol, 1,6-2,2,4-trimethylhexanediol, 1,10-decanediol, hydrogenated dilinoleylglycol, hydrogenated diolelylglycol; and cycloaliphatic diols such as 1,3-cyclohexanediol, 1,4-dimethylolcyclohexane-, 1,4-cyclohexanediol, 1,3-dimethylolcyclohexane, 1,4-endo methylene-2-hydroxy-5-hydroxymethyl cyclohexane, and polyalkylene glycols. The diols used in the reaction may be a single diol or a mixture of diols depending on the properties desired in the finished product. Polycarbonate intermediates which are hydroxyl terminated are generally those known to the art and in the literature. Suitable carbonates are selected from alkylene carbonates composed of a 5 to 7 member ring. Suitable carbonates for use herein include ethylene carbonate, trimethylene carbonate, tetramethylene carbonate, 1,2-propylene carbonate, 1,2-butylene carbonate, 2,3-butylene carbonate, 1,2-ethylene carbonate, 1,3-pentylene carbonate, 1,4-pentylene carbonate, 2,3-pentylene carbonate, and 2,4-pentylene carbonate. Also, suitable herein are dialkylcarbonates, cycloaliphatic carbonates, and diarylcarbonates. The dialkylcarbonates can contain 2 to 5 carbon atoms in each alkyl group and specific examples thereof are diethylcarbonate and dipropylcarbonate. Cycloaliphatic carbonates, especially dicycloaliphatic carbonates, can contain 4 to 7 carbon atoms in each cyclic structure, and there can be one or two of such structures. When one group is cycloaliphatic, the other can be either alkyl or aryl. On the other hand, if one group is aryl, the other can be alkyl or cycloaliphatic. Examples of suitable

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diarylcarbonates, which can contain 6 to 20 carbon atoms in each aryl group, are diphenylcarbonate, ditolylcarbonate, and dinaphthylcarbonate.

[0040] Suitable polysiloxane polyols include alpha-omega-hydroxyl or amine or carboxylic acid or thiol or epoxy terminated polysiloxanes. Examples include poly(dimethylsiloxane) terminated with a hydroxyl or amine or carboxylic acid or thiol or epoxy group. In some embodiments, the polysiloxane polyols are hydroxyl terminated polysiloxanes. In some embodiments, the polysiloxane polyols have a number-average molecular weight in the range from 300 to 5,000, or from 400 to 3,000.

[0041] Polysiloxane polyols can be obtained by the dehydrogenation reaction between a polysiloxane hydride and an aliphatic polyhydric alcohol or polyoxyalkylene alcohol to introduce the alcoholic hydroxy groups onto the polysiloxane backbone. Suitable examples include alpha-omega-hydroxypropyl terminated poly(dimethylsiloxane) and alpha-omega-amino propyl terminated poly(dimethylsiloxane), both of which are commercially available materials. Further examples include copolymers of the poly(dimethylsiloxane) materials with a poly(alkylene oxide).

[0042] Suitable polyester polyols may also be referred to hydroxyl terminated polyester intermediates and can include linear polyesters having a number average molecular weight (M_n) of from about 500 to about 10,000, from about 700 to about 5,000, or from about 700 to about 4,000, and generally have an acid number generally less than 1.3 or less than 0.5. The molecular weight is determined by assay of the terminal functional groups and is related to the number average molecular weight. The polyester intermediates may be produced by (1) an esterification reaction of one or more glycols with one or more dicarboxylic acids or anhydrides or (2) by transesterification reaction, i.e., the reaction of one or more glycols with esters of dicarboxylic acids. Mole ratios generally in excess of more than one mole of glycol to acid are preferred so as to obtain linear chains having a preponderance of terminal hydroxyl groups. The dicarboxylic acids of the desired polyester can be aliphatic, cycloaliphatic, aromatic, or combinations thereof. Suitable dicarboxylic acids which may be used alone or in mixtures generally have a total of from 4 to 15 carbon atoms and include: succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic, dodecanedioic, isophthalic, terephthalic, cyclohexane dicarboxylic, and the like. Anhydrides of the above dicarboxylic acids such as phthalic anhydride, tetrahydrophthalic anhydride, or the like, can also be used. Adipic acid is often a preferred

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acid. The glycols which are reacted to form a desirable polyester intermediate can be aliphatic, aromatic, or combinations thereof, including any of the glycol described above in the chain extender section, and have a total of from 2 to 20 or from 2 to 12 carbon atoms. Suitable examples include ethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,3-
5 butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 2,2-dimethyl-1,3-propanediol, 1,4-cyclohexanedimethanol, decamethylene glycol, dodecamethylene glycol, and mixtures thereof.

[0043] Suitable polyester polyols can include polyester diols derived from caprolactone monomers. The polycaprolactone polyester polyols are terminated by
10 primary hydroxyl groups. Suitable polycaprolactone polyester polyols may be made from ϵ -caprolactone and a bifunctional initiator such as di ethylene glycol, 1,4-butanediol, or any of the other glycols and/or diols listed herein. In some embodiments, the polycaprolactone polyester polyols are linear polyester diols derived from caprolactone monomers.

15 **[0044]** Useful examples include CAPA™ 2202A, a 2,000 number average molecular weight (Mn) linear polyester diol, and CAPA™ 2302A, a 3,000 Mn linear polyester diol, both of which are commercially available from Ingevity Corporation. These materials may also be described as polymers of 2-oxepanone and 1,4-butanediol.

[0045] Polycaprolactone polyester polyols may be prepared from 2-oxepanone and
20 a diol, where the diol may be 1,4-butanediol, di ethylene glycol, monoethylene glycol, 1,6-hexanediol, 2, 2-dimethyl- 1,3 -propanediol, or any combination thereof. In some embodiments, the diol used to prepare the polycaprolactone polyester polyol is linear. The polycaprolactone polyester polyol can prepared from 1,4-butanediol. In some
25 embodiments, the polycaprolactone polyester polyol has a number average molecular weight from 500 to 10,000, or from 500 to 5,000, or from 1,000 or even 2,000 to 4,000 or even 3,000.

[0046] Suitable polyester polyols can include polyamide oligomers. The term
30 "polyamide oligomer" refers to an oligomer with two or more amide linkages, or sometimes the amount of amide linkages will be specified. A subset of polyamide oligomers is telechelic polyamides. Telechelic polyamides are polyamide oligomers with high percentages, or specified percentages, of two functional groups of a single chemical type, e.g., two terminal amine groups (meaning either primary, secondary, or mixtures), two

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terminal carboxyl groups, two terminal hydroxyl groups (again meaning primary, secondary, or mixtures), or two terminal isocyanate groups (meaning aliphatic, aromatic, or mixtures).

5 **[0047]** In particular, the polyol component can have average molecular weight from 1,000 to 3,000, preferably from 1,000 to 2,000.

The chain extender component

10 **[0048]** The TPU compositions described herein are made using: (c) a chain extender component that includes at least one diol chain extender of the general formula HO-(CH₂)_x-OH wherein x is an integer from 2 to 6 or even from 4 to 6. In other embodiments, x is 4.

[0049] Suitable examples include, but are not limited to, ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, 1,4-butanediol (BDO), 1,6-hexanediol (HDO), 1,3-butanediol, 1,5-pentanediol, as well as mixtures thereof.

15 **[0050]** In some embodiments, the chain extender includes BDO, HDO, or a combination thereof.

[0051] In some embodiments, the chain extender includes BDO.

[0052] In some embodiments, the chain extender essentially consists of or even consist of BDO.

20 **[0053]** In some embodiments, the chain extender component may further include one or more additional chain extenders. These additional chain extenders are not overly limited and may include diols (other than those described above), diamines, and combinations thereof.

25 Polyurethane compositions

[0054] The TPU compositions of the invention can be prepared by processes which are conventional in the art for the synthesis of polyurethane elastomers such as, but not limited to, a batch process or a one-shot technique. In the batch process, the components, i.e., the diisocyanate(s), the polyol(s), and the chain extender(s), as well as the catalyst(s)
30 and any other additive(s), if desired, are introduced into a container, mixed, dispensed into trays and allowed to cure. The cured TPU can then be granulated and pelletized. The one-shot procedure is performed in an extruder, e.g., single screw, twin screw,

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wherein the formative components, introduced individually or as a mixture into the extruder, and reacted at a temperature generally in one embodiment from about 100°C to about 300°C, and in another embodiment from about 150°C to about 250°C, and even from about 150°C to about 240°C.

5 **[0055]** One or more polymerization catalysts may be present during the polymerization reaction. Generally, any conventional catalyst can be utilized to react the diisocyanate with the polyol intermediates or the chain extender. 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
10 conventional tertiary amines known from the prior art, e.g. triethylamine, dimethylcyclohexylamine, 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 acetylacetonate, tin compounds, e.g. stannous diacetate, stannous dioctoate, stannous
15 dilaurate, or the dialkyltin salts of aliphatic carboxylic acids, e.g. dibutyltin diacetate, dibutyltin dilaurate, or the like. The amounts usually used of the catalysts are from 0.0001 to 0.1 part by weight per 100 parts by weight of polyhydroxy compound (b).

[0056] The TPU composition may be prepared, for example, by a process that includes the step of (I) reacting: a) the polyisocyanate component described above; b) the
20 polyol component described above; and c) the chain extender component described above.

[0057] The process may further include the step of: (II) mixing the TPU composition of step (I) with one or more blend components, including one or more additional TPU materials and/or polymers, including any of those described above.

25 **[0058]** The process may further include the step of: (II) mixing the TPU composition of step (I) with one or more additional additives selected from the group consisting of pigments, UV stabilizers, UV absorbers, antioxidants, lubricity agents, heat stabilizers, hydrolysis stabilizers, cross-linking activators, flame retardants, layered silicates, fillers, colorants, reinforcing agents, adhesion mediators, impact strength modifiers, and
30 antimicrobials.

[0059] The process may further include the step of: (II) mixing the TPU composition of step (I) with one or more blend components, including one or more additional TPU

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materials and/or polymers, including any of those described above, and/or the step of:
(III) mixing the TPU composition of step (I) with one or more additional additives selected
from the group consisting of pigments, UV stabilizers, UV absorbers, antioxidants,
lubricity agents, heat stabilizers, hydrolysis stabilizers, cross-linking activators, flame
retardants, layered silicates, fillers, colorants, reinforcing agents, adhesion mediators,
impact strength modifiers, and antimicrobials.

[0060] In some embodiments, the TPU compositions of the invention can have a
Shore A hardness, as measured by ASTM D2240, of from 60 to 100, or from 75 to 100,
or of from 80 to 100, or particularly from 85 to 95, or more particularly of 90.

[0061] In some embodiments, the TPU compositions of the invention can have a
Shore D hardness, as measured by ASTM D2240 of from 50 to 70, particularly from 55
to 65, more particularly of 60.

[0062] The TPU compositions of the invention have a hard segment content of from
22 to 65 wt.% based on the total weight of the composition. The term "hard segment" as
used herein refers to the combined weight of polyisocyanate component and the chain
extender component. The hard segment content of the TPU may be calculated by adding
the weight percent content of polyisocyanate and chain extender in the TPU and dividing
that total by the sum of the weight percent contents of the chain extender, polyisocyanate,
and polyol in the TPU.

[0063] In particular, the hard segment content can be from 25 to 65 wt.%, or from 30
to 65 wt.% based on the total weight of the composition.

[0064] More particularly, the hard segment content can be from 45 to 65 wt.%, based
on the total weight of the composition.

[0065] In particular, the hard segment content can be from 45 to 50 wt.%, which
further improves the processability of the TPU, i.e. the ability of the TPU to be thermally
processed into parts with acceptable properties, such as, but not-limited to chemical,
mechanical, and thermal properties expected of the polymer, and especially, quality of
the final part, optical properties, low amount of defects, and desired texture of the final
part. The remainder of the TPU is derived from the polyol component.

[0066] The molar ratio of the chain extender to the polyol of the TPU is not limited so
long as the hardness and snap back requirements are met. In some embodiments, the

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molar ratio of the chain extender to the polyol of the TPU (chain extender:polyol) is from 5.9:1 to 10:1 with the preferred range from 6.4:1 to 7.8:1.

[0067] Advantageously, the TPU compositions of the present invention show superior resistance to environmental stress cracking, in particular when exposed to chemical reagents, more particularly organic solvents such as isopropanol. Environmental stress cracking (ESC) can be determined by methods well known by the skilled in the art such as ASTM D543-21. The working EXAMPLES (section Test methods) herein provide a detailed description of an assay suitable to determine stress cracking.

[0068] In one embodiment environmental stress cracking (ESC) is evaluated by bending an injection molded bar over a fixture. Test specimens are made by injection molding rectangular bars with dimensions of 12.5 x 1.3 x 0.032 cm (l x w x h). After processing, samples are conditioned at room temperature and 50% RH +/- 10% for a minimum of two days. The specimens are mounted in a strain fixture and fixed in position. In the strain fixture, specimens are bent over a curved surface with a radius of 0.724 cm. This radius and the thickness of the specimens produce a high level of strain on the outer surface of the specimen. A tissue in the chemical reagent (isopropyl alcohol) is then wiped on the top of the specimen (area with most curvature). Cracking is determined by visible inspection by eye.

[0069] Therefore, the technology described herein also provides a method of improving the environmental stress cracking of a TPU composition, material and/or article. The method involves using the polyisocyanate component described above, the polyol component described above, and the chain extender component described above to prepare a TPU material, in place of or in combination with the polyol and chain extender of the original TPU, resulting in a TPU composition, material and/or article with superior resistance to environmental stress cracking.

[0070] Also included herein are TPU compositions, wherein the hard segment content is 27 wt.% and the the weight ratio from aliphatic diisocyanate (a)(i) to cyclic aliphatic diisocyanate (a)(ii) is 3:1.

[0071] Also included herein are TPU compositions, wherein the hard segment content is 30 wt.% and the the weight ratio from aliphatic diisocyanate (a)(i) to cyclic aliphatic diisocyanate (a)(ii) is from 1:1 to 3:1, particularly from 1.5 to 3.1.

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[0072] Also included herein are TPU compositions wherein the hard segment content is 45 wt. % and the weight ratio from aliphatic diisocyanate (a)(i) to cyclic aliphatic diisocyanate (a)(ii) is 3:1.

5 **[0073]** Also included herein are TPU compositions wherein the hard segment content is from 50 to 60 wt.% and the weight ratio from aliphatic diisocyanate (a)(i) to cyclic aliphatic isocyanate (a)(ii) is from 1:1 to 2:1, preferably from 1:1 to 1.5:1.

[0074] The TPU compositions of the invention can comprise the reaction product of at least:

10 a) a polyisocyanate comprising hexamethylene diisocyanate (HDI) and 4,4'-diisocyanato dicyclohexylmethane (H12MDI) wherein the concentration of hexamethylene diisocyanate (HDI) is at least 50 wt.% based on the total weight of the polyisocyanate component;

b) a polyol comprising at least a hydroxyl-terminated poly(butadiene) (HTPB); and,

15 c) a chain extender comprising at least one diol chain extender of the general formula $\text{HO}-(\text{CH}_2)_x\text{-OH}$ wherein x is an integer from 2 to about 6;

wherein the thermoplastic polyurethane composition has a hard segment of from 45 to 65 wt.% based on the total weight of the composition, wherein the hard segment content is defined as the combined weight of the polyisocyanate component a) and the chain extender component c).

20 **[0075]** The TPU compositions of the invention can comprise the reaction product of at least:

25 a) a polyisocyanate comprising hexamethylene diisocyanate (HDI) and 4,4'-diisocyanato dicyclohexylmethane (H12MDI) wherein the concentration of hexamethylene diisocyanate (HDI) is 50 wt.% based on the total weight of the polyisocyanate component;

b) a polyol comprising at least a hydroxyl-terminated poly(butadiene) (HTPB); and,

30 c) a chain extender comprising at least one diol chain extender of the general formula $\text{HO}-(\text{CH}_2)_x\text{-OH}$ wherein x is an integer from 2 to about 6;

wherein the thermoplastic polyurethane composition has a hard segment of from 60 to 65 wt.% based on the total weight of the composition, wherein the hard segment content is defined as the combined weight of the polyisocyanate component a) and the chain extender component c). In this embodiment, the hydroxyl-terminated poly(butadiene)

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(HTPB) can particularly be the compound of Formula (I) wherein X is from 15 to 20, Y is from 1 to 5 and Z is from 15 to 25, preferably wherein X is 17, Y is 3 and Z is 20.

[0076] The TPU compositions of the invention can comprise the reaction product of at least:

- 5 a) a polyisocyanate comprising hexamethylene diisocyanate (HDI) and 4,4'-diisocyanato dicyclohexylmethane (H12MDI) wherein the concentration of hexamethylene diisocyanate (HDI) is of at least 50 wt.% based on the total weight of the polyisocyanate component;
- b) a polyol comprising at least a hydroxyl-terminated poly(butadiene) (HTPB); and,
- 10 c) a chain extender comprising at least one diol chain extender of the general formula $\text{HO}-(\text{CH}_2)_x-\text{OH}$ wherein x is an integer from 2 to about 6;

wherein the thermoplastic polyurethane composition has a hard segment of from 45 to 55 wt.% based on the total weight of the composition, wherein the hard segment content is defined as the combined weight of the polyisocyanate component a) and the chain extender component c). In particular, the concentration of HDI can be more than 50 wt.%, more particularly at least 60 wt.%. In this embodiment, the hydroxyl-terminated poly(butadiene) (HTPB) can particularly be the compound of Formula (I) wherein X is from 10 to 15, Y is from 5 to 10 and Z is from 35 to 45, preferably wherein X is 13, Y is 7 and Z is 40.

20 **[0077]** The TPU compositions of the invention can comprise the reaction product of at least:

- a) a polyisocyanate comprising hexamethylene diisocyanate (HDI) and 4,4'-diisocyanato dicyclohexylmethane (H12MDI) wherein the concentration of hexamethylene diisocyanate (HDI) is of from 75 to 100 wt.% based on the total weight of the polyisocyanate component;
- 25 b) a polyol comprising at least a hydroxyl-terminated poly(butadiene) (HTPB); and,
- c) a chain extender comprising at least one diol chain extender of the general formula $\text{HO}-(\text{CH}_2)_x-\text{OH}$ wherein x is an integer from 2 to about 6;

wherein the thermoplastic polyurethane composition has a hard segment of 45 wt.% based on the total weight of the composition, wherein the hard segment content is defined as the combined weight of the polyisocyanate component a) and the chain extender component c). In this embodiment, the hydroxyl-terminated poly(butadiene) (HTPB) can

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particularly be the compound of Formula (I) wherein X is from 10 to 15, Y is from 5 to 10 and Z is from 35 to 45, preferably wherein X is 13, Y is 7 and Z is 40.

[0078] The TPU compositions of the invention can comprise the reaction product of at least:

- 5 a) a polyisocyanate comprising hexamethylene diisocyanate (HDI) and 4,4'-diisocyanato dicyclohexylmethane (H12MDI) wherein the concentration of hexamethylene diisocyanate (HDI) is of 60 wt.% based on the total weight of the polyisocyanate component;
- b) a polyol comprising at least a hydroxyl-terminated poly(butadiene) (HTPB); and,
- 10 c) a chain extender comprising at least one diol chain extender of the general formula $\text{HO}-(\text{CH}_2)_x-\text{OH}$ wherein x is an integer from 2 to about 6;

wherein the thermoplastic polyurethane composition has a hard segment of 50 wt.% based on the total weight of the composition, wherein the hard segment content is defined as the combined weight of the polyisocyanate component a) and the chain extender component c). In this embodiment, the hydroxyl-terminated poly(butadiene) (HTPB) can particularly be the compound of Formula (I) wherein X is from 10 to 15, Y is from 5 to 10 and Z is from 35 to 45, preferably wherein X is 13, Y is 7 and Z is 40.

[0079] The TPU compositions of the invention can comprise the reaction product of at least:

- 20 a) a polyisocyanate component comprising 1,4-bis(isocyanatomethyl)cyclohexane (1,4-H6XDI) and 4,4'-diisocyanato dicyclohexylmethane (H12MDI) wherein the concentration of 1,4-bis(isocyanatomethyl)cyclohexane (1,4-H6XDI) is at least 60 wt.% based on the polyisocyanate component;
- b) a polyol comprising at least a hydroxyl-terminated poly(butadiene) (HTPB); and,
- 25 c) a chain extender comprising at least one diol chain extender of the general formula $\text{HO}-(\text{CH}_2)_x-\text{OH}$ wherein x is an integer from 2 to about 6;

wherein the thermoplastic polyurethane composition has a hard segment of 60 wt.% based on the total weight of the composition, wherein the hard segment content is defined as the combined weight of the polyisocyanate component a) and the chain extender component c). In this embodiment, the hydroxyl-terminated poly(butadiene) (HTPB) can particularly be the compound of Formula (I) wherein X is from 15 to 20, Y is from 1 to 5 and Z is from 15 to 25, preferably wherein X is 17, Y is 3 and Z is 20.

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[0080] The TPU compositions of the invention can comprise the reaction product of at least:

[0081] a polyisocyanate comprising hexamethylene diisocyanate (HDI) and 4,4'-diisocyanato dicyclohexylmethane (H12MDI) wherein the concentration of hexamethylene diisocyanate (HDI) is at least 50 wt.%, or more than 50 wt.%, based on the total weight of the polyisocyanate component;

[0082] a polyol comprising at least a hydroxyl-terminated poly(butadiene) (HTPB); and,

[0083] a chain extender comprising at least one diol chain extender of the general formula $\text{HO}-(\text{CH}_2)_x\text{-OH}$ wherein x is an integer from 2 to 6;

[0084] wherein the thermoplastic polyurethane composition has a hard segment of from 22 to 75 wt.% based on the total weight of the composition, wherein the hard segment content is defined as the combined weight of the polyisocyanate component a) and the chain extender component c).

[0085] The TPU compositions of the invention can comprise the reaction product of at least:

a) a polyisocyanate comprising hexamethylene diisocyanate (HDI) and 4,4'-diisocyanato dicyclohexylmethane (H12MDI) wherein the concentration of hexamethylene diisocyanate (HDI) is at least 50 wt.%, or more than 50 wt.%, based on the total weight of the polyisocyanate component;

b) a polyol comprising at least a hydroxyl-terminated poly(butadiene) (HTPB); and,

c) a chain extender comprising at least one diol chain extender of the general formula $\text{HO}-(\text{CH}_2)_x\text{-OH}$ wherein x is an integer from 2 to 6;

wherein the thermoplastic polyurethane composition has a hard segment of from 27 to 75 wt.% based on the total weight of the composition, wherein the hard segment content is defined as the combined weight of the polyisocyanate component a) and the chain extender component c).

[0086] The TPU compositions of the invention can comprise the reaction product of at least:

a) a polyisocyanate comprising hexamethylene diisocyanate (HDI) and 4,4'-diisocyanato dicyclohexylmethane (H12MDI) wherein the concentration of

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hexamethylene diisocyanate (HDI) is at least 50 wt.%, or more than 50 wt.% based on the total weight of the polyisocyanate component;

- b) a polyol comprising at least a hydroxyl-terminated poly(butadiene) (HTPB); and
- c) a chain extender comprising at least one diol chain extender of the general formula

5 HO-(CH₂)_x-OH wherein x is an integer from 2 to 6;

wherein the thermoplastic polyurethane composition has a hard segment of from 30 to 75 wt.% based on the total weight of the composition, wherein the hard segment content is defined as the combined weight of the polyisocyanate component a) and the chain extender component c).

10 **[0087]** The TPU compositions of the invention can comprise the reaction product of at least:

- a) a polyisocyanate comprising hexamethylene diisocyanate (HDI) and 4,4'-diisocyanato dicyclohexylmethane (H12MDI) wherein the concentration of hexamethylene diisocyanate (HDI) is from more than 50 wt.% to less than 75 wt.%

15 based on the total weight of the polyisocyanate component;

- b) a polyol comprising at least a hydroxyl-terminated poly(butadiene) (HTPB); and
- c) a chain extender comprising at least one diol chain extender of the general formula

20 HO-(CH₂)_x-OH wherein x is an integer from 2 to 6;
wherein the thermoplastic polyurethane composition has a hard segment of from 30 to 75 wt.% based on the total weight of the composition, wherein the hard segment content is defined as the combined weight of the polyisocyanate component a) and the chain extender component c).

Other components or ingredients

25 **[0088]** The described compositions include the TPU components described above and also include one or more additional components. These additional components include other polymeric materials that may be blended with the TPU described herein. These additional components also include one or more additives that may be added to the TPU, or blend containing the TPU, to impact the properties of the composition.

30 **[0089]** The TPU described herein may also be blended with one or more other polymers. The polymers with which the TPU described herein may be blended are not overly limited. In some embodiments, the described compositions include a two or more

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of the described TPU materials. In some embodiments, the compositions include at least one of the described TPU materials and at least one other polymer, which is not one of the described TPU materials. In some embodiments, the described blends will have the same combination of properties described above for the TPU composition. In other
5 embodiments, the TPU composition will of course have the described combination of properties, while the blend of the TPU composition with one or more of the other polymeric materials described above may or may not.

[0090] Polymers that may be used in combination with the TPU materials described herein also include more conventional TPU materials such as non-caprolactone
10 polyester-based TPU, polyether-based TPU, or TPU containing both non-caprolactone polyester and polyether groups. Other suitable materials that may be blended with the TPU materials described herein include polycarbonates, polyolefins, styrenic polymers, acrylic polymers, polyoxymethylene polymers, polyamides, polyphenylene oxides, polyphenylene sulfides, polyvinylchlorides, chlorinated polyvinylchlorides, polylactic
15 acids, or combinations thereof.

[0091] Polymers for use in the blends described herein include homopolymers and copolymers. Suitable examples include: (i) a polyolefin (PO), such as polyethylene (PE), polypropylene (PP), polybutene, ethylene propylene rubber (EPR), polyoxyethylene (POE), cyclic olefin copolymer (COC), or combinations thereof; (ii) a styrenic, such as
20 polystyrene (PS), acrylonitrile butadiene styrene (ABS), styrene acrylonitrile (SAN), styrene butadiene rubber (SBR or HIPS), polyalphamethylstyrene, styrene maleic anhydride (SMA), styrene-butadiene copolymer (SBC) (such as styrene-butadiene-styrene copolymer (SBS) and styrene-ethylene/butadiene-styrene copolymer (SEBS)), styrene-ethylene/propylene-styrene copolymer (SEPS), styrene butadiene latex (SBL),
25 SAN modified with ethylene propylene diene monomer (EPDM) and/or acrylic elastomers (for example, PS-SBR copolymers), or combinations thereof; (iii) a thermoplastic polyurethane (TPU) other than those described above; (iv) a polyamide, such as Nylon™, including polyamide 6,6 (PA66), polyamide 1,1 (PA11), polyamide 1,2 (PA12), a copolyamide (COPA), or combinations thereof; (v) an acrylic polymer, such as polymethyl
30 acrylate, polymethylmethacrylate, a methyl methacrylate styrene (MS) copolymer, or combinations thereof; (vi) a polyvinylchloride (PVC), a chlorinated polyvinylchloride (CPVC), or combinations thereof; (vii) a polyoxymethylene, such as polyacetal; (viii) a

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polyester, such as polyethylene terephthalate (PET), polybutylene terephthalate (PBT), copolyesters and/or polyester elastomers (COPE) including polyether-ester block copolymers such as glycol modified polyethylene terephthalate (PETG), polylactic acid (PLA), polyglycolic acid (PGA), copolymers of PLA and PGA, or combinations thereof; (ix) a polycarbonate (PC), a polyphenylene sulfide (PPS), a polyphenylene oxide (PPO), or combinations thereof; or combinations thereof.

[0092] In some embodiments, these blends include one or more additional polymeric materials selected from groups (i), (iii), (vii), (viii), or some combination thereof. In some embodiments, these blends include one or more additional polymeric materials selected from group (i). In some embodiments, these blends include one or more additional polymeric materials selected from group (iii). In some embodiments, these blends include one or more additional polymeric materials selected from group (vii). In some embodiments, these blends include one or more additional polymeric materials selected from group (viii).

[0093] The additional additives suitable for use in the TPU compositions described herein are not overly limited. Suitable additives include pigments, UV stabilizers, UV absorbers, antioxidants, lubricity agents, heat stabilizers, hydrolysis stabilizers, cross-linking activators, flame retardants, layered silicates, radio opacifiers, such as barium sulfate, tungsten metal, non-oxide bismuth salts, fillers, colorants, reinforcing agents, adhesion mediators, impact strength modifiers, antimicrobials, and any combination thereof.

[0094] In some embodiments, the additional component is a flame retardant. Suitable flame retardants are not overly limited and may include a boron phosphate flame retardant, a magnesium oxide, a dipentaerythritol, a polytetrafluoroethylene (PTFE) polymer, or any combination thereof. In some embodiments, this flame retardant may include a boron phosphate flame retardant, a magnesium oxide, a dipentaerythritol, or any combination thereof. A suitable example of a boron phosphate flame retardant is BUDIT®-326, commercially available from Budenheim USA, Inc. When present, the flame retardant component may be present in an amount from 0 to 10 weight percent of the overall TPU composition, in other embodiments from 0.5 to 10, or from 1 to 10, or from 0.5 or 1 to 5, or from 0.5 to 3, or even from 1 to 3 weight percent of the overall TPU composition.

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[0095] The TPU compositions described herein may also include additional additives, which may be referred to as a stabilizer. The stabilizers may include antioxidants such as phenolics, phosphites, thioesters, and amines, light stabilizers such as hindered amine light stabilizers and benzothiazole UV absorbers, and other process stabilizers and combinations thereof. In one embodiment, the preferred stabilizer is Irganox®-1010 from BASF and Naugard®-445 from Chemtura. The stabilizer is used in the amount from about 0.1 weight percent to about 5 weight percent, in another embodiment from about 0.1 weight percent to about 3 weight percent, and in another embodiment from about 0.5 weight percent to about 1.5 weight percent of the TPU composition.

[0096] In addition, various conventional inorganic flame-retardant components may be employed in the TPU composition. Suitable inorganic flame retardants include any of those known to one skilled in the art, such as metal oxides, metal oxide hydrates, metal carbonates, ammonium phosphate, ammonium polyphosphate, calcium carbonate, antimony oxide, clay, mineral clays including talc, kaolin, wollastonite, nanoclay, montmorillonite clay which is often referred to as nano-clay, and mixtures thereof. In one embodiment, the flame-retardant package includes talc. The talc in the flame-retardant package promotes properties of high limiting oxygen index (LOI). The inorganic flame retardants may be used in the amount from 0 to about 30 weight percent, from about 0.1 weight percent to about 20 weight percent, in another embodiment about 0.5 weight percent to about 15 weight percent of the total weight of the TPU composition.

[0097] Still further optional additives may be used in the TPU compositions described herein. The additives include colorants, antioxidants (including phenolics, phosphites, thioesters, and/or amines), antiozonants, stabilizers, inert fillers, lubricants, inhibitors, hydrolysis stabilizers, light stabilizers, hindered amines light stabilizers, benzotriazole UV absorber, heat stabilizers, stabilizers to prevent discoloration, dyes, pigments, inorganic and organic fillers, reinforcing agents and combinations thereof.

[0098] All of the additives described above may be used in an effective amount customary for these substances. The non-flame retardants additives may be used in amounts of from about 0 to about 30 weight percent, in one embodiment from about 0.1 to about 25 weight percent, and in another embodiment about 0.1 to about 20 weight percent of the total weight of the TPU composition.

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[0099] These additional additives can be incorporated into the components of, or into the reaction mixture for, the preparation of the TPU resin, or after making the TPU resin. In another process, all the materials can be mixed with the TPU resin and then melted or they can be incorporated directly into the melt of the TPU resin.

5

Articles

[00100] The TPU compositions described herein may be used in the preparation of one or more articles. The specific type of articles that may be made from the TPU compositions described herein are not overly limited.

[00101] Therefore, the invention further provides an article made with the TPU compositions described herein. Examples include but are not limited to medical applications, for example, where the TPU described herein may be used in pacemaker heads; angiography, angioplasty, epidural, thermal dilation, and urology catheters; catheter connectors; medical tubing; cartilage replacement, hair replacement, joint replacement, and the like, as well as used in, personal care applications, pharmaceutical applications, health care product applications, or any other number of applications. In some embodiments, these articles are prepared by extruding, injection molding, or any combination thereof.

[00102] In some embodiments, the article is a medical device or a medical component. Particularly, the medical device or component is selected from the group consisting of a cardiac pacing lead insulation, neuromodulation lead insulation, heart valve, hydrocephalus shunt, biliary stent, balloon stent, and orthopaedic article.

[00103] 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.

EXAMPLES

Abbreviations

30 HS = hard segment

HDI= hexamethylene diisocyanate

H12MDI= 4,4'-diisocyanate dicyclohexylmethane.

1,4-H6XDI= 1,4-bis(isocyanatomethyl)cyclohexane

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BDO= 1,4-butanediol

PTEMG= poly(tetramethylene ether) glycol

HPBD= hydroxyl-terminated poly(butadiene)

5 Test methods

 a. Hardness

[00104] Hardness was determined with a durometer according to ASTM D2240.

 b. Environmental stress cracking

10 **[00105]** Resistance to stress cracking was determined by visual inspection of samples after exposure to isopropyl alcohol as determined by ASTM D543-21. The test specimens were made by injection molding rectangular bars with dimensions of 12.5 x 1.3 x 0.032 cm (l x w x h). Samples were equilibrated after processing. The specimens were mounted in a strain fixture and fixed in position. In the strain fixture, specimens were bent over a curved surface with a radius of 0.724 cm. This radius and the thickness of the specimens
15 produce a high level of strain on the outer surface of the specimen. A tissue was then soaked in the chemical reagent (isopropyl alcohol) and then wiped on the top of the specimen (area with most curvature). Cracking was typically instantaneous and visible by eye. Multiple wipes with saturated tissue were repeated. If cracking occurred, subsequent
20 wipes increased depth and density of cracking. Specimens left in the strained position for multiple days after exposure did not show signs of either starting to crack (no cracks initially) or showed deepening cracks (if cracked initially).

EXAMPLE 1

25 **[00106]** A series of thermoplastic polymers comprising H12MDI or HDI and H12MDI or HDI as diisocyanates were used for preparing test samples. The chain extender was BDO. Detailed composition is set out in Table 1. Stress cracking, hardness and processability of extruded films were determined.

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TABLE 1

ID	HS (wt. %)	HDI in HDI/H12MDI blend (wt. %)	Polyol	Cracking	Measured Durometer (peak)	Processability (Extruded film)
A	60	0	Nisso GI- 1000 ¹	Yes	65.2D	Good (No gels, clear)
B		15		Yes	n/a	n/a
C		30		Yes	n/a	n/a
D		50		No	56.8D	Poor (Opaque, leathery)
E	65	50		No	56.3D	Poor (Gels, opaque, difficult to pelletize)
F	70	50		Yes	43.6D	Fail (Not processable)
G	45	0	Krasol HLBH- P2000 ²	Yes	85.1A	Good (No gels, clear)
H		15		Yes	n/a	n/a
I		30		Yes	74.8A	Good (No gels, clear)
J		50		Fine cracks	81.1A	Good (No gels, clear)
K		75		No	80.0A	Good (No gels, clear)
M		100		No	79.9A	Good (No gels, hazy)
N	50	60		No	93.8A	Good

ID	HS (wt. %)	HDI in HDI/H12MDI blend (wt. %)	Polyol	Cracking	Measured Durometer (peak)	Processability (Extruded film)
	55					(No gels, slightly hazy)
L		75		No	89.5A	Poor (Hazy, leathery)
O		60		No	87.2A	Poor (Hazy, leathery)
P		75		No	88.9A	Fail (Tacky, opaque, difficult processing)

¹ Nisso™ GI-1000 both-end hydroxyl group-terminated polybutadiene from Nippon Soda Co., LTD.

² Krasol® HLBH-P2000 Hydrogenated Hydroxyl Terminated Polyol from Cray Valley.

5 **[00107]** TPU compositions comprising an amount of hard segment from 45 to 65 wt.% and an amount of HDI of at least 50 wt.% showed better tolerance to isopropanol.

EXAMPLE 2

10 **[00108]** A series of thermoplastic polymers comprising H12MDI or 1,4-H6XDI and H12MDI or 1,4-H6XDI as diisocyanates were used for preparing test samples. BDO was used as chain extender. Detailed composition is set out in Table 2. Stress cracking, hardness and processability by injection molding were determined.

TABLE 2

ID	HS (wt.%)	1,4-H6XDI in 1,4-H6XDI/H12MDI blend (wt.%)	Polyol	Cracking	Measured Durometer ASTM D2240 (peak / 5 sec)	Processability (Injection Molded)
P	60	0	Nisso GI- 1000 ¹	Yes	65.2D	Good
Q		50		Yes	57.4D / 48.7D	Good
R		60		No	52.9D / 42.5D	Good
S		100		No	66.8D / 59.5D	Good
T	70	50		Yes	64D / 57.5D	Good

¹ Nisso™ GI-1000 both-end hydroxyl group-terminated polybutadiene from Nippon Soda Co., LTD.

5 **[00109]** TPU compositions comprising 60 wt.% of hard segment and 60 or 100 wt.% of 1,4-H6XDI based on the total weight of the polyisocyanate component showed higher resistance to cracking caused by isopropanol.

EXAMPLE 3

10 **[00110]** A series of thermoplastic polymers comprising H12MDI or HDI and H12MDI or HDI as diisocyanates were used for preparing test samples. The chain extender was BDO. Detailed composition is set out in Table 3. Stress cracking, hardness and processability of extruded films were determined.

TABLE 3

ID	HS (wt.%)	HDI in HDI/H12MDI blend (wt. %)	Polyol	Cracking	Measured Durometer (peak)	Processability (Extruded film)
U	22	75	Krasol HLBH- P2000 ¹	No	73.3A	Good (no gels, clear)

ID	HS (wt. %)	HDI in HDI/H12MDI blend (wt. %)	Polyol	Cracking	Measured Durometer (peak)	Processability (Extruded film)
W	30	0	Krasol HLBH- P3000 ¹	Yes	85.1A	Good (no gels, clear)
X		25		Yes	57.6A	Good (no gels, clear)
Y		50		Yes	68.1A	Good (no gels, clear)
Z		60		No	71.9A	Good (no gels, clear)
AA		75		No	71.9A	OK (hazy)

¹ Krasol® HLBH-P2000 and HLBH-P3000 Hydrogenated Hydroxyl Terminated Polyol from Cray Valley.

EXAMPLE 4

5 **[00111]** Chemical resistance and biostability through 24h nitric acid exposure was determined for different TPU samples. The composition of TPU samples is summarized in Table 4.

TABLE 4

	C1 ¹	C2 ^{1,2}	C3 ¹	AB
	wt. %			
HPBD			55	55
PTMEG 1000MW		50		
PTMEG 2000MW	74			
H12MDI	22	2	35	8
HDI		34		24
1,4 BDO	4	14	10	13

¹ Comparative examples

² Representative TPU of WO2016054320A1.

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[00112] Biostability, was evaluated by exposing TPU film sections to 35% nitric acid for 24 hours followed by polymer property characterization. Nitric acid can act as a hydrolytic and oxidative agent on the polymer. The resistance to hydrolytic and oxidative degradation are important markers of biostability. The chemical resistance was determined by the degree of chemical and physical changes to the polymer by comparing material properties of the TPU films with no exposure to nitric acid and after 24 hours submerged in room temperature nitric acid. The test specimens were made by extruding film and cutting sections with dimensions of the specimens defined in ASTM D1708. The specimens were placed in a 20ml vial and submerged in 20ml of 35% nitric acid for up to 24 hours. After that time period, the TPU film specimens were removed and rinsed thoroughly with deionized water to remove acid. The specimens were dried under vacuum for at least 18 hours. Specimens were then characterized by GPC for changes in molecular weight, ASTM D1708 for changes in tensile properties, and by light and scanning electron microscopy for visual and surface changes. The properties after nitric acid exposure were compared to the properties of the TPU film with no exposure to nitric acid.

[00113] Property changes after 24hr nitric acid exposure are summarized in Table 5.

TABLE 5

	C1	C2	C3	AB
% Change in Tensile Strength at Break	-68%	-60%	-11%	-20%
% Change in Elongation at Break	22%	-45%	-4%	-23%
% Change in Mn average Molecular weight	-90%	-31%	-16%	5%

Visual/Surface Changes	Deformed shape, yellowness, surface cracks and pitting	Yellowness, minor surface erosion	No major changes	No major changes
ESC Resistant ¹	Yes	Yes	No	Yes

¹Resistance after exposure to isopropyl alcohol

[00114] Various aspects and embodiments of the present invention are also defined by the following numbered clauses:

- 5
1. A thermoplastic polyurethane composition comprising the reaction product of at least:
a) a polyisocyanate comprising at least 50 wt.% based on the total weight of the polyisocyanate component of (i) an aliphatic diisocyanate having from 6 to 10 carbon atoms;
b) a polyol comprising at least a hydroxyl-terminated poly(butadiene) (HTPB); and,
10 c) a chain extender comprising at least one diol chain extender of the general formula HO-(CH₂)_x-OH wherein x is an integer from 2 to 6;
wherein the thermoplastic polyurethane composition has a hard segment of from 45 to 65 wt.% based on the total weight of the composition, wherein the hard segment content is defined as the combined weight of the polyisocyanate component a) and
15 the chain extender component c).
2. A thermoplastic polyurethane composition according to clause 1, wherein the aliphatic diisocyanate (i) is a linear aliphatic diisocyanate.
- 20 3. A thermoplastic polyurethane composition according to clause 2, wherein the aliphatic diisocyanate (i) is hexamethylene diisocyanate (HDI).
4. A thermoplastic polyurethane composition according to clause 1 wherein the aliphatic diisocyanate (i) is a cyclic aliphatic diisocyanate.
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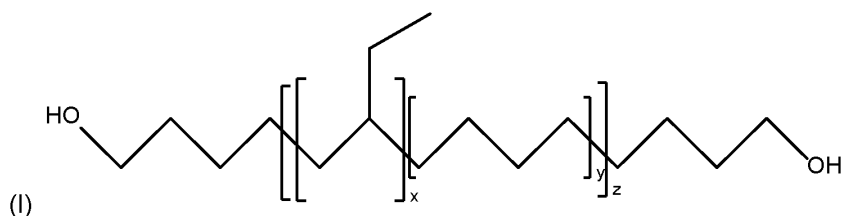
5. A thermoplastic polyurethane composition according to clause 4 wherein the aliphatic diisocyanate (i) is 1,4-bis(isocyanatomethyl)cyclohexane (1,4-H6XDI).
- 5 6. A thermoplastic polyurethane composition according to any of the previous clauses wherein the concentration of aliphatic isocyanate (i) is from 55 to 75 wt.% based on the total weight of the polyisocyanate component.
- 10 7. A thermoplastic polyurethane composition according to any of the previous clauses wherein the hard segment content is from 45 to 60 wt.% based on the total weight of the composition, preferably from 45 to 50 wt.%.
- 15 8. A thermoplastic polyurethane composition according to any one of the previous clauses, wherein the polyisocyanate (a) further comprises (ii) a cyclic aliphatic isocyanate different from the aliphatic diisocyanate (a)(i).
9. A thermoplastic polyurethane composition according to clause 8, wherein the cyclic aliphatic isocyanate (a)(ii) is 4,4'-diisocyanato dicyclohexylmethane (H12MDI).
- 20 10. A thermoplastic polyurethane composition according to clause 8 or 9, wherein the weight ratio from aliphatic diisocyanate (a)(i) to cyclic aliphatic isocyanate (a)(ii) is from 1:1 to 3:1.
- 25 11. A thermoplastic polyurethane composition according to clause 10, wherein the hard segment content is 45 wt.% and the weight ratio from aliphatic diisocyanate (a)(i) to cyclic aliphatic diisocyanate (a)(ii) is 3:1.
- 30 12. A thermoplastic polyurethane composition according to clause 10, wherein the hard segment content is from 50 to 60 wt.% and the weight ratio from aliphatic diisocyanate (a)(i) to cyclic aliphatic isocyanate (a)(ii) is from 1:1 to 2:1, preferably from 1:1 to 1.5:1.

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13. A thermoplastic polyurethane composition according to any one of the previous clauses, wherein the polyol component has an average molecular weight from 1,000 to 3,000, preferably from 1,000 to 2,000.

5 14. A thermoplastic polyurethane composition according to any one of the previous clauses, wherein the hydroxyl-terminated poly(butadiene) is a hydroxyl-terminated hydrogenated polybutadiene.

10 15. A thermoplastic polyurethane composition according to clause 14, wherein the hydroxyl-terminated hydrogenated polybutadiene is a compound selected from Formula (I):



15 wherein X is an integer from 10 to 20, Y is an integer from 1 to 10, and Z is an integer from 10 to 60.

16. A thermoplastic polyurethane composition according to clause 15, wherein Z is an integer from 20 to 40.

20 17. A thermoplastic polyurethane composition according to clause 15 or 16 wherein X is from 10 to 15, Y is from 5 to 10 and Z is from 35 to 45, preferably wherein X is 13, Y is 7 and Z is 40.

25 18. A thermoplastic polyurethane composition according to clause 15 or 16 wherein X is from 15 to 20, Y is from 1 to 5 and Z is from 15 to 25, preferably wherein X is 17, Y is 3 and Z is 20.

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19. A thermoplastic polyurethane composition according to any one the previous clauses wherein the chain extender (c) is BDO.
- 5 20. A thermoplastic polyurethane composition according to any one the previous clauses having a Shore A hardness of from 60 to 100 or a Shore D hardness from 50 to 60 as measured by ASTM D2240.
- 10 21. A thermoplastic polyurethane composition according to any one the previous clauses having a Shore A hardness of from 80 to 100, preferably from 85 to 95 as measured by ASTM D2240.
- 15 22. A thermoplastic polyurethane composition according to any one the previous clauses having a Shore D hardness of from 50 to 70, preferably from 55 to 65 as measured by ASTM D2240.
- 20 23. A thermoplastic polyurethane composition according to any one the previous clauses, wherein the thermoplastic polyurethane composition does not exhibit visible cracking when exposed to isopropyl alcohol as determined by ASTM D543-21.
- 25 24. A thermoplastic polyurethane composition according to any one the previous clauses further comprising one or more additional additives selected from the group consisting of pigments, UV stabilizers, UV absorbers, antioxidants, lubricity agents, heat stabilizers, hydrolysis stabilizers, cross-linking activators, flame retardants, layered silicates, fillers, colorants, reinforcing agents, adhesion mediators, impact strength modifiers, and antimicrobials.
- 30 25. An article comprising the thermoplastic polyurethane composition of any one of clauses 1 to 24.
26. An article according to clause 25, wherein the article is a medical device or a medical device component.

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27. An article according to clause 26, wherein the medical device or component is selected from the group consisting of a cardiac pacing lead insulation, neuromodulation lead insulation, heart valve, hydrocephaly shunt, biliary stent, balloon stent, and orthopedics article.

28. A process of making a thermoplastic polyurethane composition according to any one of clauses 1 to 23, said process comprising the step of reacting:

a) a polyisocyanate comprising at least 50 wt.% based on the total weight of the polyisocyanate component of (i) an aliphatic diisocyanate having from 6 to 10 carbon atoms;

b) a polyol comprising at least a hydroxyl-terminated poly(butadiene) (HTPB); and

c) a chain extender comprising at least one diol chain extender of the general formula $\text{HO}-(\text{CH}_2)_x-\text{OH}$ wherein x is an integer from 2 to 6;

wherein the amount of hard segment of the composition is from 45 to 65 wt.% based on the total weight of the composition.

[00115] 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.

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CLAIMS:

1. A thermoplastic polyurethane composition comprising the reaction product of at least:
 - a) a polyisocyanate comprising at least 50 wt.% based on the total weight of the polyisocyanate component of (i) an aliphatic diisocyanate having from 6 to 10 carbon atoms;
 - b) a polyol comprising at least a hydroxyl-terminated poly(butadiene) (HTPB); and
 - c) a chain extender comprising at least one diol chain extender of the general formula $\text{HO}-(\text{CH}_2)_x-\text{OH}$ wherein x is an integer from 2 to about 6;wherein the thermoplastic polyurethane composition has a hard segment of from 22 to 65 wt.% based on the total weight of the composition, wherein the hard segment content is defined as the combined weight of the polyisocyanate component a) and the chain extender component c).
2. A thermoplastic polyurethane composition according to claim 1, wherein the aliphatic diisocyanate (i) is a linear aliphatic diisocyanate.
3. A thermoplastic polyurethane composition according to claim 2, wherein the aliphatic diisocyanate (i) is hexamethylene diisocyanate (HDI).
4. A thermoplastic polyurethane composition according to claim 1, wherein the aliphatic diisocyanate (i) is a cyclic aliphatic diisocyanate.
5. A thermoplastic polyurethane composition according to claim 4, wherein the aliphatic diisocyanate (i) is 1,4-bis(isocyanatomethyl)cyclohexane (1,4-H6XDI).
6. A thermoplastic polyurethane composition according to any of the previous claims wherein the concentration of aliphatic isocyanate (i) is from 55 to 75 wt.% based on the total weight of the polyisocyanate component.
7. A thermoplastic polyurethane composition according to any one of the previous claims wherein the hard segment content is from 30 to 65 wt.%,

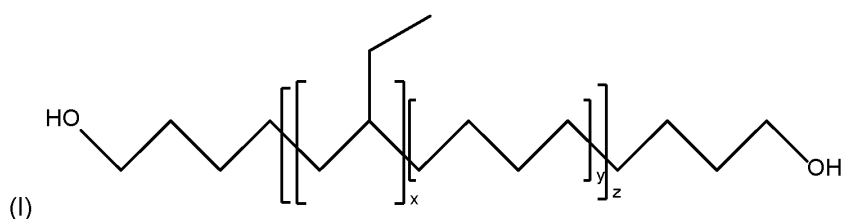
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8. A thermoplastic polyurethane composition according to any one of the previous claims wherein the hard segment content is from 45 to 65 wt.%,
- 5 9. A thermoplastic polyurethane composition according to any one of the previous claims wherein the hard segment content is from 45 to 60 wt.% based on the total weight of the composition, preferably from 45 to 50 wt.%.
- 10 10. A thermoplastic polyurethane composition according to any one of the previous claims, wherein the polyisocyanate (a) further comprises (ii) a cyclic aliphatic isocyanate different from the aliphatic diisocyanate (a)(i).
- 15 11. A thermoplastic polyurethane composition according to claim 10, wherein the cyclic aliphatic isocyanate (a)(ii) is 4,4'-diisocyanato dicyclohexylmethane (H12MDI).
12. A thermoplastic polyurethane composition according to claim 10 or 11, wherein the weight ratio from aliphatic diisocyanate (a)(i) to cyclic aliphatic isocyanate (a)(ii) is from 1:1 to 3:1.
- 20 13. A thermoplastic polyurethane composition according to claim 12, wherein the hard segment content is 45 wt.% and the weight ratio from aliphatic diisocyanate (a)(i) to cyclic aliphatic diisocyanate (a)(ii) is 3:1.
- 25 14. A thermoplastic polyurethane composition according to claim 12, wherein the hard segment content is from 50 to 60 wt.% and the weight ratio from aliphatic diisocyanate (a)(i) to cyclic aliphatic isocyanate (a)(ii) is from 1:1 to 2:1, preferably from 1:1 to 1.5:1.
- 30 15. A thermoplastic polyurethane composition according to any one of the previous claims, wherein the polyol component has an average molecular weight from 1,000 to 3,000, preferably from 1,000 to 2,000.

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16. A thermoplastic polyurethane composition according to any one of the previous claims wherein the hydroxyl-terminated poly(butadiene) is a hydroxyl-terminated hydrogenated polybutadiene.

5 17. A thermoplastic polyurethane composition according to claim 16, wherein the hydroxyl-terminated hydrogenated polybutadiene is a compound selected from Formula (I):



10 wherein X is an integer from 10 to 20, Y is an integer from 1 to 10, and Z is an integer from 10 to 60.

15 18. A thermoplastic polyurethane composition according to claim 17, wherein Z is an integer from 20 to 40.

19. A thermoplastic polyurethane composition according to claim 17 or 18 wherein X is from 10 to 15, Y is from 5 to 10 and Z is from 35 to 45, preferably wherein X is 13, Y is 7 and Z is 40.

20 20. A thermoplastic polyurethane composition according to claim 17 or 18 wherein X is from 15 to 20, Y is from 1 to 5 and Z is from 15 to 25, preferably wherein X is 17, Y is 3 and Z is 20.

25 21. A thermoplastic polyurethane composition according to any one the previous claims wherein the chain extender (c) is BDO.

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22. A thermoplastic polyurethane composition according to any one the previous claims having a Shore A hardness of from 60 to 100 or a Shore D hardness from 50 to 60 as measured by ASTM D2240.
- 5 23. A thermoplastic polyurethane composition according to any one the previous claims having a Shore A hardness of from 80 to 100, preferably from 85 to 95 as measured by ASTM D2240.
- 10 24. A thermoplastic polyurethane composition according to any one the previous claims having a Shore D hardness of from 50 to 70, preferably from 55 to 65 as measured by ASTM D2240.
- 15 25. A thermoplastic polyurethane composition according to any one the previous claims, wherein the thermoplastic polyurethane composition does not exhibit visible cracking when exposed to isopropyl alcohol as determined by ASTM D543-21.
- 20 26. A thermoplastic polyurethane composition according to any one the previous claims further comprising one or more additional additives selected from the group consisting of pigments, UV stabilizers, UV absorbers, antioxidants, lubricity agents, heat stabilizers, hydrolysis stabilizers, cross-linking activators, flame retardants, layered silicates, fillers, colorants, reinforcing agents, adhesion mediators, impact strength modifiers, and antimicrobials.
- 25 27. An article comprising the thermoplastic polyurethane composition of any one of claims 1 to 26.
28. An article according to claim 27 wherein the article is a medical device or a medical device component.
- 30 29. An article according to claim 28, wherein the medical device or component is selected from the group consisting of a cardiac pacing lead insulation,

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neuromodulation lead insulation, heart valve, hydrocephaly shunt, biliary stent, balloon stent, and orthopedics article.

- 5 30. A process of making a thermoplastic polyurethane composition, said process comprising the step of reacting:
- a) a polyisocyanate comprising at least 50 wt.% based on the total weight of the polyisocyanate component of (i) an aliphatic diisocyanate having from 6 to 10 carbon atoms;
- 10 b) a polyol comprising at least a hydroxyl-terminated poly(butadiene) (HTPB); and
- c) a chain extender comprising at least one diol chain extender of the general formula $\text{HO}-(\text{CH}_2)_x-\text{OH}$ wherein x is an integer from 2 to 6;
- wherein the amount of hard segment of the composition is from 22 to 65 wt.% based on the total weight of the composition.
- 15 31. A process of making a thermoplastic polyurethane composition according to claim 30, wherein the thermoplastic polyurethane composition is a composition as defined in any one of claims 1 to 26.
- 20 32. The process of claims 30 or 31, wherein the amount of hard segment of the composition is from 30 to 65 wt.% based on the total weight of the composition.
- 25 33. The process of any one of claims 30 to 32, wherein the amount of hard segment of the composition is from 45 to 65 wt.% based on the total weight of the composition.