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(54) Title: THERMOPLASTIC POLYURETHANE COMPOSITION

(57) Abstract: The present invention relates to novel thermoplastic polyurethane (TPU) compositions made from aliphatic polyisocyanates, such as 1,4-bis(isocyanatomethyl)cyclohexane. The present invention provides for TPUs which exhibit high temperature and chemical resistance. The present invention also relates to an article made from the TPU composition disclosed herein.



TITLE

THERMOPLASTIC POLYURETHANE COMPOSITION

FIELD OF THE INVENTION

5 **[0001]** The present invention relates to thermoplastic polyurethane (TPU) compositions which can be used in articles where a TPU having high heat resistance and high chemical resistance, and in some cases, transparency or high gloss, are desirable.

BACKGROUND OF THE INVENTION

10 **[0002]** It is often desirable for articles made from thermoplastic polyurethanes to have high heat resistance and good chemical resistance. Such articles include, but are not limited to molded articles used in both the interior and exterior of automobiles, as well as electronics and related components such as cell phones, tablets, watch bands, etc. In addition, desirable appearance and finish is important
15 for many articles. Smooth, transparent, glossy finishes are desirable for many applications such as automotive applications, both in the interior, on parts such as dashboard consoles, shifter handles, and radio controls, and in the exterior on parts such as headlamps and roof components. Transparent, glossy finishes are also desirable for applications such as surface protection films, for example, paint
20 protection films, and in electronic devices, for example for mobile phone casings. Often, a glossy transparent finish is provided by placing a coating on the part. It would be desirable to have a thermoplastic polyurethane to create molded articles that have high heat resistance and chemical resistance that, in some embodiments, are also capable of providing a smooth, glossy, transparent finish.

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SUMMARY OF THE INVENTION

[0003] The present invention provides a thermoplastic polyurethane (TPU) which comprises the reaction product of (1) an aliphatic polyisocyanate, (2) a chain extender, and (3) a polyol.

30 **[0004]** More particularly, the present invention further provides a thermoplastic polyurethane (TPU) which comprises the reaction product of (1) an aliphatic

polyisocyanate, wherein the aliphatic polyisocyanate comprises 1,4-bis(isocyanatomethyl)cyclohexane, (2) a chain extender; and (3) a polyol.

[0005] In one embodiment, the invention provides a thermoplastic polyurethane (TPU) which comprises the reaction product of (1) an aliphatic polyisocyanate, wherein the aliphatic polyisocyanate comprises 1,4-bis(isocyanatomethyl)cyclohexane, (2) a chain extender, wherein the chain extender comprises an aliphatic glycol having 2 to 20 carbon atoms; and (3) a polyol, wherein the polyol comprises a polyeseter polyol.

[0006] In one embodiment, the invention provides a thermoplastic polyurethane (TPU) which comprises the reaction product of (1) an aliphatic polyisocyanate, wherein the aliphatic polyisocyanate comprises 1,4-bis(isocyanatomethyl)cyclohexane, (2) a chain extender, wherein the chain extender comprises an aliphatic glycol having 2 to 20 carbon atoms; and (3) a polyol, wherein the polyol comprises a polycaprolactone polyol.

[0007] In one embodiment, the invention provides a thermoplastic polyurethane (TPU) which comprises the reaction product of (1) an aliphatic polyisocyanate, wherein the aliphatic polyisocyanate comprises 1,4-bis(isocyanatomethyl)cyclohexane, (2) a chain extender, wherein the chain extender comprises an aliphatic glycol having 2 to 20 carbon atoms; and (3) a polyol, wherein the polyol comprises a polycarbonate polyol.

[0008] In one embodiment, the invention provides a thermoplastic polyurethane (TPU) which comprises the reaction product of (1) an aliphatic polyisocyanate, wherein the aliphatic polyisocyanate comprises 1,4-bis(isocyanatomethyl)cyclohexane, (2) a chain extender, wherein the chain extender comprises an aliphatic glycol having 2 to 20 carbon atoms; and (3) a polyol, wherein the polyol comprises a polyether polyol.

[0009] In one embodiment, the invention provides a thermoplastic polyurethane (TPU) which comprises the reaction product of (1) an aliphatic polyisocyanate, wherein the aliphatic polyisocyanate comprises 1,4-bis(isocyanatomethyl)cyclohexane, (2) a chain extender, wherein the chain extender comprises an aliphatic glycol having 2 to 20 carbon atoms; and (3) a polyol, wherein

the polyol comprises a polyester polyol, a polycaprolactone polyol, a polycarbonate polyol, a polyether polyol, or mixtures thereof.

[0010] The present invention further discloses a process of making the TPUs, comprising reacting (1) an aliphatic polyisocyanate, wherein the aliphatic polyisocyanate comprises 1,4-bis(isocyanatomethyl)cyclohexane, (2) a chain extender, and (3) a polyol. The chain extender and polyol components may be selected from any of the chain extenders or polyols discussed herein or combinations thereof. The TPU may be prepared by any known or hereafter developed methods for making TPU.

[0011] The present invention further discloses an article which comprises the described TPU.

[0012] The invention further discloses a method of increasing the heat and chemical resistance of an article, where the article comprises an effective amount of a TPU wherein the TPU comprises the reaction product of (1) an aliphatic polyisocyanate, wherein the aliphatic polyisocyanate comprises 1,4-bis(isocyanatomethyl)cyclohexane, (2) a chain extender, and (3) a polyol. The chain extender and polyol components may be selected from any of the chain extenders or polyols described herein or combinations thereof.

[0013] In another embodiment, the invention further discloses a method of making a transparent or glossy TPU, where the TPU comprises the reaction product of (1) an aliphatic polyisocyanate, wherein the aliphatic polyisocyanate comprises 1,4-bis(isocyanatomethyl)cyclohexane (2) a chain extender, and (3) a polyol. The chain extender and polyol components may be selected from any of the chain extenders or polyols described herein or combinations thereof.

[0014] In one embodiment, the TPU of the invention is transparent. In one embodiment, the TPU of the present invention has a Shore D hardness greater than 40D, for example, greater than 50D, and further for example, greater than 55D. In one embodiment the TPU of the invention retains at least 50% of its initial gloss after a chemical resistance test, such as a sunscreen cream resistance test as described herein.

In another embodiment, the TPU of the invention has a gloss rating of at least 70 gloss units as measured by a Picogloss Model 503 glossometer from Erichsen at a 20° angle for a 2mm thick molded part. In another embodiment, the TPU of the invention has a

gloss rating of at least 70 gloss units as measured by a Picogloss Model 503 glossometer from Erichsen at a 20° angle for a 2mm thick molded part and retains at least 90% of its initial gloss after a chemical resistance test (such as a sunscreen cream resistance test). In still another embodiment, the TPU of the invention has a gloss rating of at least 70 gloss units as measured by a Picogloss Model 503 glossometer from Erichsen at a 20° angle for a 2mm thick molded part, retains at least 90% of its initial gloss after a chemical resistance test (such as a sunscreen cream resistance test), and shows no visible surface deformation after a sunscreen cream resistance test. In another embodiment, the TPU composition of the present invention has a 30% or less weight increase after immersion in solvent for 72 hours.

[0015] The present invention also provides an article made from a thermoplastic polyurethane (TPU) wherein the TPU comprises the reaction product of (1) an aliphatic polyisocyanate, wherein the aliphatic polyisocyanate comprises 1,4-bis(isocyanatomethyl)cyclohexane, (2) a chain extender; and (3) a polyol.

[0016] In one embodiment, the present invention provides an article made from a thermoplastic polyurethane (TPU) wherein the TPU comprises the reaction product of (1) an aliphatic polyisocyanate, wherein the aliphatic polyisocyanate comprises 1,4-bis(isocyanatomethyl)cyclohexane, (2) a chain extender; and (3) a polyol, wherein the polyol comprises a polyester polyol.

[0017] In one embodiment, the present invention provides an article made from a thermoplastic polyurethane (TPU) wherein the TPU comprises the reaction product of (1) an aliphatic polyisocyanate, wherein the aliphatic polyisocyanate comprises 1,4-bis(isocyanatomethyl)cyclohexane, (2) a chain extender; and (3) a polyol, wherein the polyol comprises a polycaprolactone polyol.

[0018] In one embodiment, the present invention provides an article made from a thermoplastic polyurethane (TPU) wherein the TPU comprises the reaction product of (1) an aliphatic polyisocyanate, wherein the aliphatic polyisocyanate comprises 1,4-bis(isocyanatomethyl)cyclohexane, (2) a chain extender; and (3) a polyol, wherein the polyol comprises a polycarbonate polyol.

[0019] In one embodiment, the present invention provides an article made from a thermoplastic polyurethane (TPU) wherein the TPU comprises the reaction product of (1) an aliphatic polyisocyanate, wherein the aliphatic polyisocyanate comprises 1,4-

bis(isocyanatomethyl)cyclohexane, (2) a chain extender; and (3) a polyol, wherein the polyol comprises a polyether polyol.

[0020] In one embodiment, the invention provides an article made from a thermoplastic polyurethane composition wherein the TPU comprises the reaction product of (1) an aliphatic polyisocyanate, wherein the aliphatic polyisocyanate comprises 1,4-bis(isocyanatomethyl)cyclohexane, (2) a chain extender; and (3) a polyol and wherein the TPU composition has a melting peak as measured by Differential Scanning Calorimetry (DSC) of at least 195 °C. The polyols may be selected from one or more of the following: polyester polyols, polycaprolactone polyols, polycarbonate polyols, polyether polyols or combinations thereof.

[0021] In one embodiment, the invention provides an article made from a thermoplastic polyurethane composition wherein the TPU comprises the reaction product of (1) an aliphatic polyisocyanate, wherein the aliphatic polyisocyanate comprises 1,4-bis(isocyanatomethyl)cyclohexane, (2) a chain extender; and (3) a polyol and wherein the TPU composition has one or more of the following properties: (a) a melting peak as measured by Differential Scanning Calorimetry (DSC) of at least 195 °C, (b) a Shore D hardness of at least 40D, (c) has a gloss rating of at least 50 gloss units as measured by a Picogloss Model 503 glossometer from Erichsen at a 20° angle for a 2mm thick molded part, (d) maintains at least 50% of its original gloss rating after a sunscreen cream resistance test (as described herein), or (e) shows no visible deformation after a sunscreen cream resistance test.

[0022] In one embodiment, the invention provides an article made from a thermoplastic polyurethane composition wherein the TPU comprises the reaction product of (1) an aliphatic polyisocyanate, wherein the aliphatic polyisocyanate comprises 1,4-bis(isocyanatomethyl)cyclohexane, (2) a chain extender; and (3) a polyol and wherein the TPU composition has one or more of the following properties: (a) a melting peak measured by DSC of at least 195 °C, (b) a Shore D hardness of at least 55D, (c) has a gloss rating of at least 70 gloss units as measured by a Picogloss Model 503 glossometer from Erichsen at a 20° angle for a 2mm thick molded part, (d) maintains at least 90% of its original gloss rating after a sunscreen cream resistance test (as described herein), or (e) shows no visible deformation after a sunscreen cream resistance test.

[0023] In another embodiment, the invention provides an article made from a thermoplastic polyurethane composition wherein the TPU comprises the reaction product of (1) an aliphatic polyisocyanate, wherein the aliphatic polyisocyanate comprises 1,4-bis(isocyanatomethyl)cyclohexane, (2) a chain extender; and (3) a polycaprolactone polyol and wherein the TPU composition has the following properties: (a) a melting peak measured by DSC of at least 195 °C, (b) a Shore D hardness of at least 55D, (c) has a gloss rating of at least 70 gloss units as measured by a Picogloss Model 503 glossometer from Erichsen at a 20° angle for a 2mm thick molded part (d) maintains at least 90% of its original gloss rating after a sunscreen cream resistance test (as described herein) as measured by a Picogloss Model 503 glossometer from Erichsen at a 20° angle for a 2mm thick molded part, and (e) shows no visible deformation after a sunscreen cream resistance test.

[0024] In another embodiment, an article made from a TPU composition in accordance with the present invention exhibits improved chemical resistance. For example, the article made from a TPU composition may have a 30% or less weight increase after immersion in solvent for 72 hours.

[0025] In still another embodiment, an article is provided, wherein the article comprises a TPU composition which comprises the reaction product of (1) an aliphatic polyisocyanate, wherein the aliphatic polyisocyanate comprises 1,4-bis(isocyanatomethyl)cyclohexane, (2) a chain extender; and (3) a polyol and wherein the TPU composition is transparent.

[0026] In one embodiment the article comprises a film useful in protecting surfaces. In another embodiment, the article comprises an automotive part. In another embodiment, the article comprises part of an electronic device such as a casing for a mobile phone. In other embodiment, the article is a watch band. In still another embodiment, the article is an eyeglass frame.

DETAILED DESCRIPTION OF THE INVENTION

[0027] The TPU of the present invention is made from the reaction of a specific combination of components to result in a TPU which exhibits a significant increase in heat resistance and chemical resistance. For example, the TPU of the present invention may exhibit increased solvent resistance. In addition, the TPU of the

present invention may also exhibit cream (such as hand lotion or sunscreen) resistance.

[0028] In one embodiment, the TPU of the present invention includes the reaction product of (1) an aliphatic polyisocyanate, wherein the aliphatic polyisocyanate comprises 1,4-bis(isocyanatomethyl)cyclohexane, (2) a chain extender, and (3) a polyol. The technique under which these reactants are polymerized to synthesize the TPU may be conducted utilizing conventional processing equipment, catalysts, and processes. However, the polymerization is conducted in a manner that will result in the desired polymer characteristics or properties. The types and levels of aliphatic polyisocyanate, polyol and chain extender, or a combination thereof can be adjusted to attain the desired set of chemical and physical characteristics for the polymer being synthesized. The polymerization techniques useful in making the TPUs of this invention include conventional methods, such as reactive extrusion, batch processing, solution polymerization, and cast polymerization.

The Aliphatic Polyisocyanate

[0029] In one embodiment, the polyisocyanate used in synthesizing the thermoplastic polyurethane is an aliphatic polyisocyanate, such as an aliphatic diisocyanate. In some embodiments, the polyisocyanate component in the present invention is essentially free of, or even completely free of aromatic diisocyanates. Moreover, the use of multifunctional isocyanate compounds, i.e., triisocyanates, etc., which cause undesirable premature crosslinking, are generally avoided and thus the amount used, if any, is generally less than 4 mole percent in one aspect, and less than 2 mole percent in another aspect, based upon the total moles of all of the various isocyanates used.

[0030] Suitable aliphatic diisocyanates include hexamethylene-1,6-diisocyanate (HDI), isophorone diisocyanate (IPDI), 1,4-cyclohexyl diisocyanate (CHDI), decane-1,10-diisocyanate, lysine diisocyanate (LDI), 1,4-butane diisocyanate (BDI), 1,4-bis(isocyanatomethyl) cyclohexane (1,4-H6XDI), and dicyclohexylmethane-4,4'-diisocyanate (H12MDI). Mixtures of two or more aliphatic polyisocyanates may be used. In some embodiments, the polyisocyanate comprise 1,4-H6HDI. In another embodiment, the polyisocyanate consists essentially of 1,4-H6XDI. In another embodiment, the polyisocyanate consists of 1,4-H6XDI. Dimers and trimers of the

above diisocyanates may also be used as well as a blend of two or more diisocyanates may be used.

The Chain Extender

[0031] The TPU compositions described herein are made using c) a chain extender component. Chain extenders include diols, diamines, and combination thereof.

[0032] Suitable chain extenders include relatively small polyhydroxy compounds, for example lower aliphatic or short chain glycols having from 2 to 20, or 2 to 12, or 2 to 10 carbon atoms. Suitable examples include ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol (DPG), 1,4-butanediol (BDO), 1,6-hexanediol (HDO), 1,3-butanediol, 1,5-pentanediol, neopentylglycol (NPG), 2-ethyl-2-butyl-1,3-propanediol (EBPD), 1,4-cyclohexanedimethanol (CHDM), 2,2-bis[4-(2-hydroxyethoxy) phenyl]propane (HEPP), hexamethylenediol, heptanediol, nonanediol, dodecanediol, 3-methyl-1,5-pentanediol, ethylenediamine, butanediamine, hexamethylenediamine, and hydroxyethyl resorcinol (HER), and the like, as well as mixtures thereof. In some embodiments, the chain extender includes BDO, HDO, 3-methyl-1,5-pentanediol, or a combination thereof. In some embodiments, the chain extender comprises BDO. Other glycols, such as aromatic glycols could be used, but in some embodiments the TPUs described herein are essentially free of or even completely free of such materials. In some embodiments, the chain extender consists essentially of BDO. Some embodiments, however, may include a co-chain extender in order to optimize properties of the TPU composition. The co-chain extender may be selected from those listed herein or other chain extenders known to those of ordinary skill in the art.

[0033] In one embodiment, the chain extender of the present invention comprises an aliphatic glycol having from 2 to 20, or 2 to 12, or 2 to 10 carbon atoms or mixtures thereof. In another embodiment, the chain extender of the present invention consists essentially of an aliphatic glycol having from 2 to 20, or 2 to 12, or 2 to 10 carbon atoms or mixtures thereof.

The Polyol

[0034] Polyols useful in the present invention include polyester polyols 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. In some embodiments, the polyester polyol is a linear polyester polyol 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 less than 1.3 or less than 0.5. The number average molecular weight (M_n) is determined by assay of the terminal functional groups which is related to the number average molecular weight. 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. The glycols which are reacted to form a desirable polyester intermediate can be aliphatic, aromatic, or combinations thereof, including any of the glycols 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-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, neopentylglycol, 1,4-cyclohexanedimethanol, decamethylene glycol, dodecamethylene glycol, and mixtures thereof.

[0035] In one embodiment, the polyol used to form the thermoplastic polyurethane composition of the invention comprises a polycaprolactone polyol. Polycaprolactone polyols useful in the technology described herein include polyester diols derived from caprolactone monomers. The polycaprolactone polyols are terminated by primary hydroxyl groups. Suitable polycaprolactone polyols may be made from ϵ -caprolactone and a bifunctional initiator such as diethylene glycol, 1,4-butanediol, or any of the other glycols and/or diols listed herein. Useful examples include CAPA™ 2202A, a 2,000 number average molecular weight (M_n) linear polyester diol, and CAPA™ 2302A, a 3,000 M_n linear polyester diol, both of which are commercially available from Perstorp Polyols Inc. These materials may also be described as polymers of 2-oxepanone and 1,4-butanediol.

[0036] The polycaprolactone polyols may be prepared from 2-oxepanone and a diol, where the diol may be 1,4-butanediol, diethylene 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 polyol is linear. In some
5 embodiments, the polycaprolactone polyol is prepared from 1,4-butanediol. In some embodiments, the polycaprolactone polyol has a number average molecular weight determined by assay of the terminal functional groups 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.

[0037] In one embodiment, the polyol component may also comprise a
10 polycarbonate polyol. Suitable hydroxyl terminated polycarbonates 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
15 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 molecule 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
20 glycol, 1,6-hexanediol, 2,2,4-trimethyl-1,6-hexanediol, 1,10-decanediol, hydrogenated dilinoleylglycol, hydrogenated dioleyleglycol, 3-methyl-1,5-pentanediol; and cycloaliphatic diols such as 1,3-cyclohexanediol, 1,4-dimethylolcyclohexane, 1,4-cyclohexanediol-, 1,3-dimethylolcyclohexane-, 1,4-endomethylene-2-hydroxy-5-hydroxymethyl cyclohexane, and polyalkylene glycols.
25 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,
30 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 diarylcarbonates, which can contain 6 to 20 carbon atoms in each aryl group, are diphenylcarbonate, ditolylcarbonate, and dinaphthylcarbonate. The various polycarbonate 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, such as from about 700 to about 10,000, from about 1,000 to about 5,000, or from about 1,000 to about 2,500.

[0038] In one embodiment, the polyol may comprise a polyether polyol. Useful polyether polyols may include polyether polyols derived from a diol or polyol having a total of from 2 to 15 carbon atoms, in some embodiments an alkyl diol or glycol which 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) comprising ethylene oxide reacted with ethylene glycol, poly(propylene glycol) comprising propylene oxide reacted with propylene glycol, poly(tetramethylene ether glycol) comprising water reacted with tetrahydrofuran which can also be described as polymerized tetrahydrofuran, and which is commonly referred to as PTMEG. In some embodiments, the polyether intermediate includes PTMEG. 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 described compositions. Typical copolyethers include the reaction product of THF and ethylene oxide or THF and propylene oxide. 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, such as from about 700 to about 10,000, from about 1,000 to about 5,000, or from about 1,000 to about 2,500. 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 and 1,000 Mn PTMEG.

[0039] In some embodiments, the polyol may include a mixture of polyols. For example, in one embodiment, the polyol component may comprise a mixture of polycaprolactone and polyether polyol. In other embodiments, the polyol may consist essentially of a polycaprolactone polyol. In another embodiment, the polyol may consist of a polycaprolactone polyol. In still other embodiments, the polyol may consist essentially of a polycarbonate polyol. In some embodiments, the polyol may comprise a polyether polyol. In other embodiments, the polyol may be substantially free of or totally free of polyether polyols.

[0040] TPU compositions made in accordance with the present invention may have a Shore D hardness of at least about 40D, for example at least about 50D, and further for example, at least about 55D. In one embodiment, the TPU composition may have a Shore D hardness of 40D to 85D, for example 55D to 80D. In one embodiment, the TPU comprises the reaction product of 25% to 60% by weight aliphatic polyisocyanate such as 1,4-bis(isocyanatomethyl) cyclohexane (1,4-H6XDI), 10% to 65% by weight polyol, and 10% to 30% by weight chain extender. The chain extender and polyol components may be selected from any of the chain extenders or polyols disclosed herein. For example, the polyol may be selected from polyether polyols, polcaprolactone polyols, polycarbonate polyols, polyether polyols or combinations thereof. In some embodiments, the TPU of the present invention comprise at least 30% by weight hard segment (polyisocyanate + chain extender), wherein the polyisocyanate is 1,4-H6XDI. In other embodiments, the TPU of the present invention comprises at least about 35% up to about 85% by weight, or even

at least 40% by weight, or even at least 50% by weight, or even at least 55% by weight hard segment.

[0041] In another aspect, the present invention further discloses a process of making the TPU, comprising reacting (1) an aliphatic polyisocyanate, wherein the polyisocyanate comprise 1,4-H6XDI, (2) a chain extender, wherein the chain extender comprises an aliphatic glycol having 2 to 20 carbon atoms, and (3) a polyol resulting in a TPU composition with high heat and chemical resistance. The chain extender and polyol components may be selected from any of the chain extenders or polyols disclosed herein.

[0042] The process to produce the TPU polymer of this invention can utilize conventional and hereafter developed TPU manufacturing equipment and known or hereafter developed processes. The three reactants (the polyol, the aliphatic polyisocyanate, and the chain extender) are reacted together to form the TPU useful in this invention.

[0043] In one embodiment, the process is a so-called "one-shot" process where all three reactants are added to an extruder reactor and reacted. The equivalent weight amount of the diisocyanate to the total equivalent weight amount of the hydroxyl containing components, that is, the polyol intermediate and the chain extender glycol, can be from about 0.95 to about 1.10, or from about 0.96 to about 1.03, and even from about 0.97 to about 1.02. An optional urethane catalyst may be used in the reaction in some embodiments.

[0044] The TPU of the present invention can also be prepared utilizing a pre-polymer process. In the pre-polymer route, the polyol intermediates are reacted with generally an equivalent excess of one or more diisocyanates to form a pre-polymer solution having free or unreacted diisocyanate therein. An optional urethane catalyst may be use in the reaction in some embodiments. 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. In another embodiment, an excess of polyol intermediate is reacted with isocyanate to form a hydroxyl-terminated prepolymer. Subsequently, a chain extender and additional isocyanate is added. The overall equivalent ratio of the total diisocyanate to the total equivalent of the polyol intermediate and the chain extender is thus from about 0.95

to about 1.10, or from about 0.96 to about 1.02 and even from about 0.97 to about 1.05. The chain extension reaction temperature is generally from about 100 °C to about 250 °C or from about 200 °C to about 250 °C. Typically, the pre-polymer route can be carried out in any conventional device including an extruder. In such
5 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
10 20 and in some embodiments at least 25.

[0045] In one embodiment, an aliphatic polyisocyanate, for example, 1,4-bis(isocyanatomethyl) cyclohexane (1,4-H6XDI), a chain extender, and a polyol are mixed on a single or twin screw extruder with multiple heat zones and multiple feed ports between its feed end and its die end. The ingredients may be added at one or
15 more of the feed ports and the resulting TPU composition that exits the die end of the extruder may be pelletized.

[0046] In one useful embodiment, the aliphatic polyisocyanate, for example 1,4-H6XDI, the chain extender, and a polyol are generally added together and reacted in accordance with standard polyurethane synthesis methodology as described herein.
20 The TPU forming components of the present invention can be melt polymerized in a suitable mixer, such as an internal mixer known as a Banbury mixer, or in an extruder. Suitable processing or polymerization temperatures are from about 100 °C to about 250 °C in one aspect, and from about 200 °C to about 250 °C in another aspect. Suitable mixing times in order to enable the various components to react and form
25 the TPU polymers of the present invention are generally from about 2 to about 10 minutes in one aspect, and from about 3 to about 5 minutes in another aspect.

[0047] Optionally, it may be desirable to utilize catalysts such as stannous and other metal carboxylates as well as tertiary amines. Examples of metal carboxylate catalysts include stannous octoate, dibutyltin dilaurate, phenyl mercuric propionate,
30 lead octoate, iron acetylacetonate, magnesium acetylacetonate, bismuth neodecanoate, and the like. Examples of tertiary amine catalysts include triethyleneamine, and the like. The amount of the one or more catalysts is low,

generally from about 50 to about 100 parts by weight per million parts by weight of the end TPU polymer formed.

[0048] The weight average molecular weight (Mw) of the TPU polymer of the present invention range from about 60,000 to about 250,000 Daltons in one aspect, and from about 100,000 to about 200,000 Daltons in another aspect. The Mw of the TPU polymer is measured according to gel permeation chromatography (GPC) against polystyrene standard.

[0049] The TPU polymers of the present invention can be mixed with various conventional additives or compounding agents, such as antioxidants, biocides, fungicides, antimicrobial agents, anti-static additives, plasticizers, fillers, extenders, flame retardants, impact modifiers, pigments, lubricants, mold release agents, rheology modifiers, UV absorbers, and the like. The level of conventional additives will depend on the final properties and cost of the desired end-use application, as is well known to those skilled in the art of compounding TPUs. These additional additives can be incorporated into the components of, or into the reaction mixture for the preparation of the TPU, or after making the TPU. In another process, all the materials can be mixed with the TPU and then melted or they can be incorporated directly into the melt of the TPU composition.

[0050] In one embodiment, the flame retardants mixed with the TPU polymer of the invention include organic flame retardants comprising a phosphinate compound based on an organic phosphinic salt. Organic phosphinates are a recent addition to the sphere of flame retardants used in engineering thermoplastics. One preferred phosphinate is marketed as the propriety compound Exolit® OP 1311, available from Clariant GmbH, Germany. An organic phosphinate is used in conjunction with other organic flame retardants in an exemplary embodiment of the flame retardant package. The phosphinate compound may be present in an exemplary embodiment of the flame retardant TPU composition in an amount from about 5 to about 40 weight percent, more preferably from about 15 to about 25 weight percent, based on the total weight of the TPU composition.

[0051] Other organic flame retardant components include organic phosphates such as triaryl phosphates, and preferably a triphenyl phosphate, and more preferably a proprietary phosphorus based flame retardant, namely NcendX® P-30 from

Albermarle Corporation. The organic phosphate may be present in an exemplary embodiment in an amount from about 5 to about 20 weight percent, more preferably from about 5 to about 10 weight percent, based on the total weight of the TPU composition.

5 **[0052]** Other organic flame retardant components include polyhydric alcohols such as pentaerythritol and dipentaerythritol. The polyhydric alcohol may be present in an exemplary embodiment in an amount from about 0.1 to about 15 weight percent, more preferably from about 2.5 to about 10 weight percent, based on the total weight of the TPU composition. The composition may further include from about 0 to about
10 10 weight percent of ammonium pentaborate or zinc borate.

[0053] In addition, various conventional inorganic flame retardant components may be employed in the flame retardant TPU. Suitable inorganic flame retardants include any of those known to those skilled in the art, such as ammonium phosphate, ammonium polyphosphate, calcium carbonate, antimony oxide, and clay including
15 montmorillonite clay which is often referred to as nano-clay. The inorganic flame retardants may be used at a level of from 0 to about 5 weight percent of the TPU composition.

[0054] Thus, in an exemplary embodiment, a flame retardant thermoplastic polyurethane composition comprises at least one thermoplastic polyurethane polymer
20 and a flame retardant package comprising an organic phosphinate compound, an organic phosphate compound, and a polyhydric alcohol. In other exemplary embodiments, inorganic flame retardant fillers may be incorporated into the flame retardant package.

[0055] In another aspect, the present invention refers to an article comprising the
25 TPU of the present invention. Articles comprising the TPU of the present invention may be any molded articles, such as injection molded articles. In one embodiment, such TPU can be used to make articles where it is desirable to have a non-yellowing, transparent, and glossy finish. In still other embodiments, the articles containing the various composition described above include any article that may be exposed to high
30 temperatures or chemicals, such as creams, including hand lotions or sunscreen creams, during use, and especially such articles which have not been made using

thermoplastic polyurethanes in the past because of such materials having insufficient high temperature resistance or chemical resistance.

[0056] The compositions of the invention or any blends thereof may be used to prepare the molded products of this invention in any molding process. The molding processes are well known to those of ordinary skill in the art and include but are not limited to, cast molding, cold forming matched-die molding, compression molding, foam molding, injection molding, gas-assisted injection molding, profile co-extrusion, profile extrusion, rotational molding, sheet extrusion, slush molding, spray techniques, thermoforming, transfer molding, vacuum forming, wet lay-up or contact molding, blow molding, extrusion blow molding, injection blow molding, and injection stretch blow molding or combinations thereof.

[0057] The compositions may be shaped into desirable end use articles by any suitable means known in the art. Thermoforming is a process of forming at least one pliable plastic sheet into a desired shape. An embodiment of a thermoforming sequence is described, however this should not be construed as limiting thermoforming methods useful with the compositions of this invention. First, an extrudate film of the composition of this invention (and any other layers or materials) is placed on a shuttle rack to hold it during heating. The shuttle rack indexes into the oven which pre-heats the film before forming. Once the film is heated, the shuttle rack indexes back to the forming tool. The film is then vacuumed onto the forming tool to hold it in place and the forming tool is closed. The forming tool can be either "male" or "female" type tools. The tool stays closed to cool the film and the tool is then opened. The shaped laminate is then removed from the tool.

[0058] In yet another embodiment of the formation and shaping process, profile co-extrusion can be used. The profile co-extrusion process parameters are as above for the blow molding process, except the die temperatures (dual zone top and bottom) range from 150 to 235 °C, the feed blocks are from 90 to 250 °C, and the water cooling tank-temperatures are from 10 to 40 °C.

[0059] In another embodiment, articles may be made by injection molding processes. In injection molding, a shaped laminate is placed into the injection molding tool. The mold is closed and the substrate material is injected into the mold. The substrate material has a melt temperature between 200 and 300 °C in one

embodiment and from 215 and 250 °C in another embodiment is injected into the mold at an injection speed of between 2 and 10 seconds. After injection, the material is packed or held at a predetermined time and pressure to make the part dimensionally and aesthetically correct. Typical time periods are from 5 to 25 seconds and pressures from 1,380 to 10,400 kPa. The mold is cooled between 10 and 70 °C to cool the substrate. The temperature will depend on the desired gloss and appearance desired. Typical cooling time is from 10 to 30 seconds, depending on part on the thickness. Finally, the mold is opened and the shaped composite article ejected.

[0060] In yet another embodiment of the invention, the compositions of this invention may be secured to a substrate material using a blow molding operation. Blow molding is particularly useful in such applications as for making closed articles such as fuel tanks and other fluid containers, playground equipment, outdoor furniture and small enclosed structures. In one embodiment of this process, compositions of this invention are extruded through a multi-layer head, followed by placement of the uncooled laminate into a parison in the mold. The mold, with either male or female patterns inside, is then closed and air is blown into the mold to form the part.

[0061] Articles made with the TPU of the current invention may also be made by adhering the TPU to or over another polymeric part, in a process known as over-molding. The over-molding process comprises the following: (a) a substrate formed from a composition comprising a polar polymer, and (b) a molded overlay formed from an inventive composition. In one embodiment, the polar polymer is a polycarbonate (PC), ABS, PC/ABS, PBT/ABS, nylon, or another TPU. The invention also provides an over-molded article comprising the following: (a) a substrate formed from an inventive composition, and (b) a molded overlay formed from a composition comprising a polar polymer.

[0062] The invention further provides for an article where the thermoplastic polyurethane composition is extruded. That is, the invention provides for an article which is made by forcing molten TPU through a die to form a shape with a fixed cross-section.

[0063] The TPU composition of the invention and any blends thereof may be formed into monolayer or multilayer films. These films may be formed by any of the

conventional techniques known in the art including extrusion, co-extrusion, extrusion coating, lamination, blowing and casting or any combination thereof. The film may be obtained by the flat film or tubular process which may be followed by orientation in a uniaxial direction or in two mutually perpendicular directions in the plane of the film. One or more of the layers of the film may be oriented in the transverse and/or longitudinal directions to the same or different extents. This orientation may occur before or after the individual layers are brought together. Typically, the films are oriented in the Machine Direction (MD) at a ratio of up to 15, preferably between 5 and 7, and in the Transverse Direction (TD) at a ratio of up to 15 preferably 7 to 9. However in another embodiment, the film is oriented to the same extent in both the MD and TD directions.

[0064] In another embodiment, the layer comprising the TPU composition of this invention or any blends thereof may be combined with one or more other layers. The other layer(s) may be any layer typically included in multilayer film structures. For example, the other layer or layers may be: (i) Polyolefins: suitable polyolefins include homopolymers or copolymers of C2 to C40 olefins, preferably C2 to C20 olefins, preferably a copolymer of an α -olefin and another olefin or α -olefin (ethylene is defined to be an α -olefin for purposes of this invention). Suitable polyolefins also include homopolyethylene, homopolypropylene, propylene copolymerized with ethylene and or butene, ethylene copolymerized with one or more of propylene, butene or hexene, and optional dienes. Suitable examples include thermoplastic polymers such as ultra low density polyethylene, very low density polyethylene, linear low density polyethylene, low density polyethylene, medium density polyethylene, high density polyethylene, polypropylene, isotactic polypropylene, highly isotactic polypropylene, syndiotactic polypropylene, random copolymer of propylene and ethylene and/or butene and/or hexene, elastomers such as ethylene propylene rubber, ethylene propylene diene monomer rubber, neoprene, and blends of thermoplastic polymers and elastomers, such as for example, thermoplastic elastomers and rubber toughened plastics; (ii) Polar Polymers: suitable polar polymers include homopolymers and copolymers of esters, amides, actates, anhydrides, copolymers of a C2 to C20 olefin, such as ethylene and/or propylene and/or butene with one or more polar monomers such as acetates, anhydrides, esters,

alcohol, and or acrylics. Preferred examples include polyesters, polyamides, ethylene vinyl acetate copolymers, and polyvinyl chloride; (iii) Cationic Polymers: suitable cationic polymers include polymers or copolymers of geminally disubstituted olefins, α -heteroatom olefins and/or styrenic monomers. Preferred geminally disubstituted olefins include isobutylene, isopentene, isoheptene, isohexane, isooctene, isodecene, and isododecene. Suitable α -heteroatom olefins include vinyl ether and vinyl carbazole, preferred styrenic monomers include styrene, alkyl styrene, para-alkyl styrene, α -methyl styrene, chloro-styrene, and bromo-para-methyl styrene. Suitable examples of cationic polymers include butyl rubber, isobutylene copolymerized with para methyl styrene, polystyrene, and poly- α -methyl styrene; (iv) Miscellaneous: other suitable layers can be paper, wood, cardboard, metal, metal foils (such as aluminum foil and tin foil), metallized surfaces, glass (including silicon oxide (SiO_x) coatings applied by evaporating silicon oxide onto a film surface), fabric, spunbonded fibers, and nonwovens (particularly polypropylene spun bonded fibers or nonwovens), and substrates coated with inks, dyes, pigments, and the like.

[0065] Films made from TPU compositions of the present invention may vary in thickness depending on the intended application, however films of a thickness from 1 to 250 μ m are usually suitable. Films intended for packaging are usually from 10 to 60 micron thick. The thickness of the sealing layer is typically 0.2 to 50 μ m. There may be a sealing layer on both the inner and outer surfaces of the film or the sealing layer may be present on only the inner or the outer surface.

[0066] In another embodiment, one more layers may be modified by corona treatment, electron beam irradiation, gamma irradiation, or microwave irradiation. In a preferred embodiment, one or both of the surface layers is modified by corona treatment.

[0067] The invention also provides an extruded sheet formed from the TPU composition of the present invention. In one embodiment, the sheet has a thickness from 10 mils to 1,000 mils, for example from 15 mils to 500 mils, and further for example from 20 mils to 100 mils.

[0068] In one embodiment, films made from the TPU composition of the present invention are used for surface protection. In one embodiment, the invention comprises a surface protection film comprising thermoplastic polyurethane which

comprises the reaction product of (1) an aliphatic polyisocyanate, wherein the aliphatic polyisocyanate comprises 1,4-bis(isocyanatomethyl)cyclohexane, (2) a chain extender; and (3) a polyol.

[0069] The TPU compositions of the present invention provide a transparent and glossy finish. The TPU composition may be used to mold various articles or as a surface protection film on various articles where a transparent and glossy finish is desirable, for example automotive applications, both in the interior, on parts such as dashboard consoles, shifter handles, and radio controls, and in the exterior on parts such as headlamps and roof components, or as paint protection films, or for electronic components, such as mobile phone casings, or even for consumer products, such as eyeglass frames, watch bands, and other wearable technology.

[0070] In another aspect, the present invention refers to a method of increasing the heat resistance and/or chemical resistance of an article, where the article comprises an effective amount of a thermoplastic polyurethane (TPU) wherein the TPU comprises the reaction product of (1) an aliphatic polyisocyanate, wherein the aliphatic polyisocyanate comprises 1,4-bis(isocyanatomethyl) cyclohexane (1,4-H6XDI), (2) a chain extender, comprising an aliphatic glycol having 2 to 20 carbon atoms, and (3) a polyol. This method includes the step of using (1) an aliphatic polyisocyanate such as 1,4-H6XDI, (2) a chain extender, and (3) a polyol in the preparation of a TPU. Any of the TPU materials described above may be used in these methods. In one embodiment, in the method of increasing the heat resistance or chemical resistance of an article, the polyol component comprises or consists essentially of a polycaprolactone polyol.

[0071] In one embodiment, the TPU composition of the invention has a melting peak as measured by Differential Scanning Calorimetry of at least 195 °C, which is indicative of the TPU compositions heat resistance. Higher melting peak temperature provides the TPU compositions with a broader service window before the TPU product begins to melt or deform.

[0072] In one embodiment, the TPU of the invention is transparent. In one embodiment the TPU of the invention retains at least 50%, or at least 65%, or at least 70%, or at least 80%, or even at least 90% of its initial gloss after a chemical resistance test, such as a sunscreen cream resistance test as described herein. In another

embodiment, the TPU of the invention has a gloss rating of at least 70 gloss units, in one embodiment, 70 – 100 gloss units, and in another embodiment, greater than 100 gloss units as measured by a Picogloss Model 503 glossometer from Erichsen at a 20° angle for a 2mm thick molded part. In another embodiment, the TPU of the invention has a gloss rating of at least 70 gloss units as measured by a Picogloss Model 503 glossometer from Erichsen at a 20° angle for a 2mm thick molded part and retains at least 90% of its initial gloss after a chemical resistance test (such as a sunscreen cream resistance test). In still another embodiment, the TPU of the invention has a gloss rating of at least 70 gloss units as measured by a Picogloss Model 503 glossometer from Erichsen at a 20° angle for a 2mm thick molded part, retains at least 90% of its initial gloss after a chemical resistance test (such as a sunscreen cream resistance test), and shows no visible surface deformation after a sunscreen cream resistance test.

[0073] Various preferred features and embodiments will be described below by way of non-limiting illustration.

[0074] The amount of each chemical component described is presented exclusive of any solvent or diluent oil, which may be customarily present in the commercial material, that is, on an active chemical basis, unless otherwise indicated. However, unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade.

[0075] Each of the documents referred to above is incorporated herein by reference, including any prior applications, whether or not specifically listed above, from which priority is claimed. The mention of any document is not an admission that such document qualifies as prior art or constitutes the general knowledge of the skilled person in any jurisdiction. 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." It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. Similarly, the ranges and amounts for each element of the invention can be used together with ranges or amounts for any of the other elements.

EXAMPLES

[0076] In the following examples, TPU compositions are synthesized from the components set forth in the tables. The Comparative Examples use H12MDI as the polyisocyanate. Inventive Examples 1 through 13 use 1,4-H6XDI as the polyisocyanate. Various properties of the prepared TPU compositions were measured. The Comparative compositions and results are summarized in Table 1, while the Inventive Examples and results are summarized in Table 2. Shore D hardness was measured according to ASTM D2240. Melting peak (as an indicator of improved heat resistance) was measured by Differential Scanning Calorimetry. Sunscreen cream resistance was measured according to the following procedure: Sample plates (obtained by injection molding, which are 2mm thick) with a smooth surface that have been conditioned for 7 days at temperatures between 18 °C and 28 °C are prepared. The following testing procedure is followed: 1. A piece of gauze is placed over the samples, covering all the test surface; 2. A cream (Rich Moisturizing Sunscreen Lotion 40 High Protection from Isdin) is applied over the gauze until all gauze holes are filled (the cream thickness is approximately 1-2mm); 3. The sample is subjected to 80 °C temperature in a convection oven for 24 hours; 4. The gauze is removed and the remains of cream cleaned with a wipe. Before evaluation, the samples are conditioned for 4 hours at temperature between 18 °C and 28 °C. Gloss, as a quantifiable indicator of chemical resistance to sunscreen cream, was measured with a Picogloss Model 503 from Erichsen at 20° angle in 2mm thick molded parts before and after the cream test. A visual assessment of surface deformation after the sunscreen cream exposure was also conducted.

Table 1

Ingredients	Comparative Ex. 1	Comparative Ex 2	Comparative Ex 3	Comparative Ex 4
Polyol	CAPA ¹	CAPA	CAPA/PTMG	PTMG ²
Polyol MW	2000	2000	1500	1000
Isocyanate	H12MDI	H12MDI	H12MDI	H12MDI
Chain Extender	BDO	BDO	BDO	BDO
% Hard Segment	44	64	68	68
Melting Peak (°C)	107	No peak	No peak	No peak
Hardness Shore D (After 1 day)	45	65	71	66
Initial Gloss 20° (Gloss Units (“GU”))	116	145	140	142
Gloss after Sunscreen Cream Test (GU)	60	33	26	15
Surface Deformation after Sunscreen Cream Test	Very high	Very high	Very high	Very high

¹ Polycaprolactone Polyol² Polytetramethylene glycol ether

Table 2

Ingredients	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9	Example 10	Example 11	Example 12	Example 13
Polyol	CAPA	CAPA	CAPA	CAPA	CAPA/ PTMG	PTMG	PPG ³	CAPA	PBA ⁴	PC ⁵	CAPA	PC	CAPA
Polyol MW	2000	2000	2000	2000	1500	1000	1000	1000	1000	2000	1000	2000	1000
Isocyanate	H6XDI	H6XD I	H6XD I	H6XD I	H6XDI	H6XDI	H6XDI	H6XDI	H6XDI	H6XD I	H6XDI	H6XDI	H6XDI
Chain Extender	BDO	BDO	BDO	BDO	BDO	BDO	BDO	BDO + 10% DPG	BDO + 10% DPG	BDO + 10% DPG	BDO + 10% EBPD	BDO + 20% EBPD	BDO + 20% DPG
% Hard Segment	38	48	59	68	64	66	66	66	66	66	66	66	79
Melting Peak (°C)	218	208	225	228	208	214	222	200	202	216	212	198	204
Hardness Shore D (After 1 day)	43	48	56	64	65	65	65	65	67	68	64	65	78
Initial Gloss 20° (GU)	20	38	72	99	71	74	82	119	53	127	105	118	99
Gloss after Sunscreen Cream Test (GU)	11	35	68	96	65	35	37	115	49	107	100	62	100
Surface Deformation after Sunscreen Cream Test	Some	Some	None	None	Some	High	High	None	None	Some	None	High	None

³ Polypropylene glycol⁴ Polybutylene diol adipate⁵ Polycarbonate polyol

[0077] As shown above, TPU compositions made according to the present invention provide higher heat resistance as well as in some cases, better resistance to certain chemicals, such as sunscreen cream. Such properties are important for applications that require a transparent and glossy finish.

5 [0078] TPU Compositions of the present invention also exhibit increased chemical resistance as illustrated by a solvent resistance test. Samples of TPU compositions were immersed in various solvents for 72 hours at room temperature. The samples were weighed before and after immersion. The results are summarized in Table 3.

Table 3

	% of weight increase after immersion		
Solvent	Acetone	MEK	Toluene
Comparative Ex. 2	70	50	55
Example 8	29	20	15

10

[0079] Example 8 showed significantly less weight increase (and thus absorption of solvent) than Comparative Example 2.

[0080] As used herein, the transitional term “comprising,” which is synonymous with “including,” “containing,” or “characterized by,” is inclusive or open-ended and does not exclude additional, un-recited elements or method steps. However, in each recitation of “comprising” herein, it is intended that the term also 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 un-recited 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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[0081] While certain representative embodiments and details have been shown for the purpose of illustrating the subject invention, it will be apparent to those skilled in this art that various changes and modifications can be made therein without departing from the scope of the subject invention. In this regard, the scope of the invention is to be limited only by the following claims.

CLAIMS

1. A thermoplastic polyurethane composition comprising the reaction product of:
(a) a polyol;
5 (b) a chain extender;
(c) a polyisocyanate, wherein the polyisocyanate comprises 1,4-bis(isocyanatomethyl)cyclohexane,
wherein the thermoplastic polyurethane composition comprises at least 30% by weight of components (b) and (c).
10
2. The thermoplastic polyurethane composition of claim 1 wherein the composition has a melting end temperature measured by differential scanning calorimetry of at least 195 °C.
- 15 3. The thermoplastic polyurethane composition of any of claims 1 or 2 wherein the composition maintains at least 50% of its initial gloss units as measured with a Picogloss Model 503 from Erichsen at 20° angle after a sunscreen cream resistance test.
- 20 4. The thermoplastic polyurethane composition of any of claims 1 to 3 wherein the composition has a Shore D Hardness of at least 40D.
5. The thermoplastic polyurethane composition of any of claims 1 to 4 wherein the composition has a Shore D Hardness of about 50D to about 85D.
25
6. The thermoplastic polyurethane composition of any of claims 1 to 5 wherein the composition has a gloss rating of at least 70 gloss units as measured with a Picogloss Model 503 from Erichsen at 20° angle.
- 30 7. The thermoplastic polyurethane composition of any of claims 1 to 6 wherein the TPU has a gloss rating of at least 70 gloss units as measured with a Picogloss Model 503 from Erichsen at 20° angle, maintains at least 90% of its original gloss after a sunscreen cream resistance test, and shows no visible surface deformation after a sunscreen cream resistance test.

8. The thermoplastic polyurethane composition of any of claims 1 to 7 wherein the polyol comprises a polyester polyol.

9. The thermoplastic polyurethane composition of any of claims 1 to 7 wherein the polyol comprises a polycaprolactone polyol.

5 10. The thermoplastic polyurethane composition of any of claims 1 to 7 wherein the polyol consists essentially of a polycaprolactone polyol.

11. The thermoplastic polyurethane composition of any of claims 1 to 7 wherein the polyol comprises a polycarbonate polyol.

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12. The thermoplastic polyurethane composition of any of claims 1 to 7 wherein the polyol comprises a polyether polyol.

13. The thermoplastic polyurethane composition of any of claims 1 to 12 wherein the polyisocyanate consists essentially of 1,4-bis(isocyanatomethyl)cyclohexane.

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14. The thermoplastic polyurethane composition of any of claims 1 to 13 wherein the thermoplastic polyurethane composition comprises at least 50% by weight of (b) and (c).

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15. The thermoplastic polyurethane composition of any of claims 1 to 14 wherein the thermoplastic polyurethane comprises 45% to 86% by weight of (b) and (c).

16. An article obtained by injection molding a thermoplastic polyurethane composition of any of claims 1 to 15.

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17. An article obtained by extruding a thermoplastic polyurethane composition of any of claims 1 to 15.

18. A surface protection film comprising the thermoplastic polyurethane composition of any of claims 1 to 15.

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19. An article obtained by 3D printing a thermoplastic polyurethane composition of any of claims 1 to 15.

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20. An article comprising:

a thermoplastic polyurethane composition comprising the reaction product of (a) a polyol, (b) a chain extender and (c) a polyisocyanate, wherein the polyisocyanate comprises 1,4-bis(isocyanatomethyl) cyclohexane, and wherein the thermoplastic polyurethane has one or more of the following properties (i) a melting peak measured by Differential Scanning Calorimetry of at least 195 °C, (ii) a Shore D hardness of at least 40D.

21. The article of claim 20, wherein the thermoplastic polyurethane further has one or more of the following properties (iii) a gloss rating of at least 50 gloss units as measured by a Picogloss Model 503 glossometer from Erichsen at a 20° angle for a 2mm thick molded part, (iv) maintains at least 90% of its original gloss rating after a sunscreen cream resistance test, (v) shows no visible deformation after a sunscreen cream resistance test, or (vi) is transparent.

22. The article of claim 20, wherein the thermoplastic polyurethane has the following properties (i) a melting peak measured by Differential Scanning Calorimetry of at least 200 °C, (ii) a Shore D hardness of at least 55D, (iii) a gloss rating of at least 70 gloss units as measured by a Picogloss Model 503 glossometer from Erichsen at a 20° angle for a 2mm thick molded part, (iv) maintains at least 90% of its original gloss rating after a sunscreen cream resistance test (as described herein), (v) shows no visible deformation after a sunscreen cream resistance test.

23. The article of claim 22 wherein the polyol consists essentially of a polycaprolactone polyol.

24. The article of any of claims 20 to 22 wherein the polyol comprises a polycaprolactone polyol.

25. The article of any of claims 20 or 21 wherein the polyol comprises a polyester polyol.

26. The article of any of claims 20 or 21 wherein the polyol comprises a polycarbonate polyol.

5 27. The article of any of claims 20 or 21 wherein the polyol comprises a polyether polyol.

29. The article of any of claims 20 to 27 wherein the thermoplastic polyurethane composition comprises at least 50% by weight of (b) and (c).

10 30. The article of any of claims 20 to 29 wherein the article is injection molded.

31. The article of any of claims 20 to 29 wherein the article is thermoformed.

15 32. The article of any of claims 20 to 29 wherein the article is extruded.

33. The article of any of claims 20 to 29 wherein the article is printed.

34. The article of any of claims 20 to 29 wherein the article comprises a film.

20 35. The article of any of claims 20 to 29 wherein the article is an automotive part, an eyeglass frame, a phone case, an electronic device case, or a paint protection film.

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A. CLASSIFICATION OF SUBJECT MATTER		
INV.	C08G18/75	C08G18/48
	C08G18/42	C08G18/44
ADD.	C08G18/66	C08G18/32
		C08G18/40
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	US 2013/053179 A1 (TARAO TOSHIYUKI [JP] ET AL) 28 February 2013 (2013-02-28) table 1	1-35
X	US 2013/053174 A1 (SHIGA KAZUYOSHI [JP] ET AL) 28 February 2013 (2013-02-28) table 1	1-35
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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 March 2017		Date of mailing of the international search report 04/04/2017
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 Lanz, Sandra

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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