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(54) Title: THERMOPLASTIC POLYURETHANE COMPOSITION

(57) Abstract: The invention relates to a thermoplastic polyurethane material that has high flex modulus, low density, and is capable of withstanding repeated cyclic deformation. The thermoplastic polyurethane composition is formed from the reaction product of a polyol component, which includes a blend of a polyether polyol, such as poly(tetramethylene ether glycol), and polybutadiene diol, a diisocyanate component, and a chain extender component.



WO 2021/050620 A1

THERMOPLASTIC POLYURETHANE COMPOSITION

Background

[0001] The utility of thermoplastic polyurethane materials for a variety of applications is being appreciated in many new industries. However, it is often difficult to find a single thermoplastic polyurethane composition that has combinations of properties that are suited for certain applications. For example, many applications will require high modulus and hardness, but also the ability to withstand cyclic deformations and varying temperature ranges. Often polyamide-co-polyethers are used for these applications because they have high flex modulus, low density, and good low temperature fatigue resistance. However, thermoplastic polyurethane compositions that have high flex modulus lack low temperature cyclic fatigue behavior and are undesirably heavy. One reason for this is because in order to achieve the high flex modulus, the hard segment content of the thermoplastic polyurethane is increased, which also increases density and glass transition temperature. The higher density and glass transition temperatures result in less desirable performance when subject to cyclic deformations. Therefore, it is object of this invention to provide a thermoplastic polyurethane composition having the unexpected combination of properties including high modulus, low density, and the ability to sustain cyclic deformations.

Summary of the Invention

[0002] The present invention is a thermoplastic polyurethane composition comprising the reaction product of a polyol component and a diisocyanate component, wherein the polyol component comprises a mixture of a polyether polyol and polybutadiene polyol. Examples of polyether polyols include poly(tetramethylene ether glycol), polypropylene glycol, polyethylene glycol, and polyoxymethylene. The polybutadiene polyol may include unsaturated polybutadiene polyols or diols or polybutadiene diol. In one embodiment, the polyol component comprises or consists of a mixture of poly(tetramethylene ether glycol) and polybutadiene polyol. In another embodiment, the polyol component comprises or consists of a mixture of poly(tetramethylene ether glycol) and unsaturated polybutadiene polyol. In still another embodiment, the polyol component comprises a polyether component that is a blend of poly(tetramethylene ether glycol) and an ethylene oxide endcapped poly(propylene glycol) and polybutadiene polyol. The thermoplastic polyurethane

composition may optionally include a chain extender component. The invention also includes articles made from the thermoplastic polyurethane composition of the invention.

Detailed Description

[0003] Thermoplastic polyurethane compositions are generally formed from the reaction product of a polyol component, a diisocyanate component, and optionally, a chain extender component. In the thermoplastic polyurethane composition of the present invention, the polyol component is a blend of polyols, wherein the blend includes a polyether polyol and a polybutadiene polyol.

The Polyol Component

[0004] The polyol component used in the thermoplastic polyurethane composition of the present invention is a blend of polyols, wherein the blend contains a polyether polyol and a polybutadiene polyol.

[0005] Polyether polyols are typically 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. 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. These

are available from BASF as PolyTHF® B, a block copolymer, and PolyTHF® R, a random copolymer.

[0006] In one embodiment, polyether polyols used in the present invention have a number average molecular weight (Mn) as determined by assay of the terminal functional groups of about 700 to about 10,000, for example, from about 1,000 to about 5,000, or even from about 1,000 to about 3,000, or even 1000 to about 2500, or even about 2000 to about 2500. In one embodiment, the number average molecular weight of the polyether polyol used in the present invention is less than 3000.

[0007] In one embodiment, the polyether polyol used in the polyol component of the present invention comprises or consists of poly(tetramethylene ether glycol). In another embodiment, the polyether polyol used in the polyol component is a blend of polyether polyols. For example, the blend of polyether polyols comprises or consists of poly(tetramethylene ether glycol) and ethylene oxide end capped poly(propylene glycol).

[0008] The polyol component of the present invention also includes a polybutadiene polyol. In one embodiment, the polybutadiene polyol is unsaturated. In one embodiment, the polybutadiene polyol comprises or consists of polybutadiene diol, which as used herein, also refers to hydroxyl terminated polybutadiene. The molecular weight of the polybutadiene polyol used to form the thermoplastic polyurethane of the present invention depends on the desired characteristics of article to be made. Polybutadiene polyols suitable for forming a thermoplastic polyurethane composition according to the present invention may have a molecular weight from about 100 to about 10,000, for example from about 300 to about 5,000, further for example from about 1,000 to about 3,000, for example, 2,000. In some embodiments, the polybutadiene polyol has an OH functionality of 2.0 to 3.0, for example, 2.0 to 2.6.

[0009] In one embodiment, the polybutadiene polyol is unsaturated, such that the polybutadiene polyol contains double bonds along the butadiene chain.

[0010] Commercially available polybutadiene polyols useful in the present invention include KRASOL™ LBH P-2000, KRASOL™ LBH 2000, and KRASOL™ HLBH P-2000 available from Cray Valley, and NISSO™ PB G 2000, NISSO™ PB-G1400, NISSO™ PB-GI1000, and NISSO PB-GI2000 available from Nippon Soda Co.

Polyisocyanate Component

[0011] The thermoplastic polyurethane compositions described herein are made using a polyisocyanate component. The polyisocyanate and/or polyisocyanate component may include one or more polyisocyanates. In some embodiments, the polyisocyanate component includes one or more diisocyanates.

[0012] Suitable polyisocyanates include aromatic diisocyanates, aliphatic diisocyanates, or combinations thereof. In some embodiments, the polyisocyanate component includes one or more aromatic diisocyanates. In some embodiments, the polyisocyanate component is essentially free of, or even completely free of, aliphatic diisocyanates. In other embodiments, the polyisocyanate component includes one or more aliphatic diisocyanates. In some embodiments, the polyisocyanate component is essentially free of, or even completely free of, aromatic diisocyanates.

[0013] Examples of useful polyisocyanates include aromatic diisocyanates such as 4,4'-methylenebis(phenyl isocyanate) (MDI), m-xylene diisocyanate (XDI), 3,3'-dimethoxy-4,4'-biphenylenediisocyanate, phenylene-1,4-diisocyanate (PDI), phenylene-1,3-diisocyanate, naphthalene-1,5-diisocyanate, 3,3'-dimethyl-4,4'-biphenylene diisocyanate (TODI), 1,5-naphthalene diisocyanate (NDI), and toluene diisocyanate (TDI); as well as aliphatic diisocyanates such as isophorone diisocyanate (IPDI), 1,4-cyclohexyl diisocyanate (CHDI), decane-1,10-diisocyanate, lysine diisocyanate (LDI), 1,4-butane diisocyanate (BDI), isophorone diisocyanate (PDI), hexane diisocyanate (HDI), 1,4-Bis (isocyanatomethyl) cyclohexane (1,4-H6XDI), and dicyclohexylmethane-4,4'-diisocyanate (H12MDI). Mixtures of two or more polyisocyanates may be used. In one embodiment, the diisocyanate used in the present invention comprises or consists of MDI.

Chain Extender Component

[0014] The thermoplastic polyurethane composition of the present invention is optionally made using a chain extender component. 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, triethylene glycol, tetraethylene glycol, propylene glycol, dipropylene glycol, 1,4-butanediol (BDO), 1,6-hexanediol (HDO), 1,3-butanediol, 1,5-pentanediol, neopentylglycol, 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), pentaspiro glycol (PSG), hydroquinone bis(2-hydroxyethyl) ether hydroquinone (HQEE), dipropylene glycol (DPG), 2-methyl-1,3-propane diol, 2-butyl-2-ethyl-1,3-propane diol (BEPD), and the like, as well as mixtures thereof. In some embodiments, the chain extender includes BDO, HDO, 3-methyl-1,5-pentanediol, or a combination thereof.

[0015] In one embodiment of the present invention, the chain extender comprises or consists of 1,4-butane diol. In another embodiment, the chain extender component comprises or consists of 2-butyl-2-ethyl-1,3-propane diol. In another embodiment, the chain extender component comprises or consists of dipropylene glycol. In still another embodiment, the chain extender comprises or consists of neopentylglycol. In another embodiment, the chain extender component comprises mixtures of chain extenders selected from 1,4-butane diol, 2-butyl-2-ethyl-1,3-propane diol, dipropylene glycol, and neopentylglycol.

[0016] The hard segment content of a thermoplastic polyurethane composition is defined as the combined weight percent of the diisocyanate component and the chain extender component. In some embodiments of the present invention, the thermoplastic polyurethanes herein have a hard segment content of 49% to 80% by weight, for example 54% to 75% by weight.

[0017] In one embodiment of the present invention, the thermoplastic polyurethane comprises the reaction product of a polyether polyol and polybutadiene polyol, a diisocyanate component, and optionally a chain extender component. In another embodiment, the thermoplastic polyurethane comprises the reaction product of a polyol component and a diisocyanate, where the polyol component comprises a mixture of a polyether polyol and polybutadiene polyol, wherein the polyether polyol is at least 50% by weight of the polyol component. In one such embodiment, the polyether polyol greater than 50% by weight of the polyol component. In another embodiment, polyol component comprises a mixture of polyether polyol and polybutadiene polyol in weight ratios from 90:10 to 40:60, for example, 80:20 to 60:40, even further for example, 70:30 to 60:40.

[0018] In another embodiment of the present invention, the thermoplastic polyurethane comprises the reaction product of a polyol component and a diisocyanate component, where the polyol component comprises or consists of a mixture of poly(tetramethylene ether glycol) and unsaturated polybutadiene diol and a diisocyanate component. In such an embodiment, the

polyol component may comprise a mixture of poly(tetramethylene ether glycol) and polybutadiene diol in weight ratios from 90:10 to 40:60, for example, 80:20 to 60:40, even further for example, 70:30 to 60:40

[0019] Thermoplastic polyurethane compositions of the present invention may be made using any process now known or hereafter developed. For example, in one embodiment, the “one-shot” process may be used, where the reactants (polyol component, diisocyanate, and optionally, the chain extender component) are added to an extruder reactor and reacted. In another embodiment, the thermoplastic polyurethane may be prepared utilizing a pre-polymer process. In the pre-polymer process, 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. 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. Typically, the pre-polymer route can be carried out in any conventional device including an extruder.

[0020] Optionally, it may be desirable to utilize catalysts such as stannous and other metal carboxylates as well as tertiary amines. Examples of suitable catalysts which in particular accelerate the reaction between the NCO groups of the diisocyanates and the hydroxy groups of the polyols and chain extenders are the conventional tertiary amines known from the prior art, e.g. triethylamine, 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 dilaurate, or the dialkyltin salts of aliphatic carboxylic acids, e.g. dibutyltin diacetate, dibutyltin dilaurate, or the like, phenyl mercuric propionate, lead octoate, iron acetylacetonate, magnesium acetylacetonate, or bismuth compounds such as bismuth octoate, bismuth laurate, and the like.

[0021] Various types of optional components can be present during the polymerization reaction, and/or incorporated into the TPU elastomer described above. These include, but are not limited to, antioxidants, biocides, compatibilizers, electro-dissipative antistatic additives, fillers/reinforcing agents, flame and fire retardants, fungicides, impact modifiers, pigments, colorants, plasticizer, polymers, rheology modifiers, slip additives, and UV stabilizers. All of the additives described above may be used in an effective amount customary for these substances.

[0022] 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.

[0023] Thermoplastic polyurethane compositions of the present invention exhibit unexpected properties including a flex modulus measured according to ASTM D790 of at least 160MPa while exhibiting the ability to withstand at least 30,000 low temperature fatigue cycles measured according to ASTM D1052 at -10°C. In some embodiments, the thermoplastic polyurethane compositions according to the present invention have a flex modulus of at least 160 MPa or even 200 MPa and exhibit the ability to withstand at least 40,000 low temperature fatigue cycles. Another unexpected property associated with the inventive thermoplastic polyurethanes of the present invention is the transparency of such materials. In one embodiment, the materials showing the unexpected flex modulus and ability to withstand low temperature fatigue cycles additionally show transparency. In one embodiment, the thermoplastic polyurethane of the present invention exhibits a haze of 22% or less as measured according to ASTM D1003 on 75mil injection molded plaques. The present invention also includes an article made with a thermoplastic polyurethane exhibiting these unique and unexpected properties and a method for making such articles by known methods such as molding or extruding.

[0024] Thermoplastic polyurethane compositions of the present invention may be used in a variety of applications, including but not limited to industrial applications including hose and tubes and wire and cables such as high-pressure tubes, wire and cable coatings/insulation, footwear applications such as running shoes, cleated shoes, winter and summer sports equipment and applications such as snowboard, ski equipment, mountain climbing equipment, kayak and rafting equipment, golf equipment, golf balls, cycling equipment, personal protective equipment and applications such as shin guards, helmet and applications in personal electronic components.

[0025] A series of thermoplastic polyurethane sample compositions were formed by reacting the components noted in Table 1. The isocyanate component for all samples is MDI.

Table 1

	Polyol component	Blend ratio	Chain extender	Hard segment (%) ¹	Hardness (D) ²	Flex modulus (MPa) ³	Low temp Fatigue (# of cycles) ⁴	Haze (%) 75 mill thickness ⁵
1	PTMEG: PBD	60:40	BDO	80		1852		
2	PTMEG: PBD	60:40	BDO	75		1805		
3	PTMEG: PBD	60:40	BDO	66	74	1140	40K+	
4	PTMEG: PBD	60:40	BDO	64	64	1007	40K+	
5	PTMEG: PBD	20:80	BDO	59		144		
6	PTMEG: PBD	40:60	BDO	59		595		
7	PTMEG: PBD	60:40	BDO	59	66	699	40K+	
8	PTMEG: PBD	70:30	BDO	59	63	543	40K+	22
9	PTMEG: PBD	80:20	BDO	59		587		
10	PTMEG: PBD	90:10	BDO	59		153		
11	PTMEG: PBD	60:40	BDO	54	55	444	40K+	
12	PTMEG: PBD	60:40	BDO	49		91		
13	PTMEG: PBD ⁶	60:40	BDO	59		383		
14	PTMEG: PBD ⁷	60:40	BDO	59		370		
15	PPG: PBD	60:40	BDO	59		350		
16	PTMEG: EO capped PPG: PBD	35:15:50	BDO	64		938		
17	PTMEG: PBD	60:40	BDO:BEPD (30:70)	54	58	228	40K+	5.3
18	PTMEG: PBD	60:40	BDO:DPG (20:80)	54	59	172	40K+	
19	PTMEG: PBD	60:40	DPG	54	60	160	40K+	
20	PTMEG: PBD	60:40	BEPD	54	62	289	40K+	
21	PTMEG: PBD	60:40	BDO:NPG: BEPD (30:20:50)	59		605		
22	PTMEG: PBD	60:40	BDO:BEPD (30:70)	59	67	553	40K+	
23	PTMEG: PBD	60:40	BDO:DPG (20:80)	59	64	362	40K+	
24	PTMEG: PBD	60:40	NPG	59		719		
25	PTMEG: PBD	60:40	BDO:NPG (10:90)	59		691		
C1	PTMEG	100	BDO	80		1951		
C2	PTMEG	100	BDO	75		1214		
C3	PTMEG	100	BDO	69	75	970	6K	2.4
C4	PTMEG	100	BDO	66		484		
C5	PTMEG	100	BDO:DPG (87:13)	66	70	423	15K	1.5
C6	PTMEG	100	BDO	64		345		
C7	PTMEG	100	BDO	62		320		
C8	PTMEG	100	BDO	59		120		
C9	PTMEG	100	BDO	58	65	116	40K+	5.9
C10	PTMEG	100	BDO	49		Low ⁸		
C11	PBD	100	BDO	80		792		100
C12	PBD	100	BDO	64		71		100

C13	PBD	100	BDO	59		Low ⁸		100
C14	PBD	100	BEPD	64		71		
C15	PBD	100	DPG	64		165		
C16	Polycaprolactone diol	100	BDO	-	65	306	20K	42.5
C17	Sebacis:BDO	100	BDO:DPG (93:7)	-	55	115	40K+	11.2

¹Hard Segment is the total weight % of the polyisocyanate component and chain extender component.

² Hardness is measured using a Durometer according to ASTM D2240.

³ Flex modulus was measured according to ASTM D790.

⁴ Low temp fatigue was measured according to ASTM D1052 at -10 °C. The flex angle was 60° and the frequency was 1.7Hz. The testing was discontinued after 40K cycles

⁵ Haze was measured according to ASTM D1003 on 75mil injection molded plaques

⁶ PBD⁶ is polybutadiene polyol with average molar mass of 2900g/mol, OH functionality of 2.4 (approx.). The isomer ratio of 1,2-vinyl, 1,4-trans and 1,4-cis is approximately 22,58 and 20% respectively. The commercial name is Polyvest HT

⁷ PBD⁷ is polybutadiene polyol with average molar mass of 2800g/mol, OH functionality of 2.4-2.6 (approx.). The ratio of 1,2-vinyl, 1,4-trans and 1,4-cis isomers is approximately 20,60 and 20% respectively. The commercial name is Poly bd R45LTO.

⁸ The samples were too soft (low flex modulus) for reliable flex modulus testing.

[0026] The results in Table 1 show that the combination of poly(tetramethylene ether glycol) and polybutadiene diol provide an unexpected and synergistic effect in terms of flexural modulus and ability to withstand cyclic deformations. It would generally be expected that the addition of polybutadiene diol to a thermoplastic polyurethane composition including a polyether polyol would lower the flex modulus, but as the data in Table 1 illustrates, the flex modulus of thermoplastic polyurethanes containing the combination is unexpectedly higher. In addition, the inventive examples are able to withstand a high number of cyclic deformations.

[0027] 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 basic and novel characteristics of the composition or method under consideration.

[0028] While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

Claims

1. A thermoplastic polyurethane comprising the reaction product of:
 - (a) a polyol component comprising a mixture of a polyether polyol and polybutadiene polyol; and
 - (b) a diisocyanate component.
2. The thermoplastic polyurethane of claim 1, wherein the polyether polyol comprises or consists of poly(tetramethylene ether glycol), polypropylene glycol, polyethylene glycol, polyoxymethylene, or mixtures thereof.
3. The thermoplastic polyurethane of claim 1 or 2, wherein the polybutadiene polyol comprises or consists of unsaturated polybutadiene polyol.
4. The thermoplastic polyurethane of any of claims 1 to 3, further comprising:
 - (c) a chain extender component.
5. The thermoplastic polyurethane of any of claims 1 to 4, wherein the thermoplastic polyurethane has a hard segment content of 49% to 80% by weight, wherein the hard segment content is defined as the combined weight of the diisocyanate component and the chain extender component.
6. The thermoplastic polyurethane of claim 5, wherein the thermoplastic polyurethane has a hard segment content of 54% to 75% by weight.
7. The thermoplastic polyurethane of any of claims 4 to 6, wherein the chain extender component is selected from 1,4-butanediol, 2-butyl-2-ethyl-1,3-propanediol, dipropylene glycol, neopentyl glycol, and mixtures thereof.
8. The thermoplastic polyurethane of any of claims 1 to 7, wherein the polyol component comprises at least 50% by weight polyether polyol.

9. The thermoplastic polyurethane of claim 8, wherein the polyol component comprises greater than 50% by weight polyether polyol.
10. The thermoplastic polyurethane of any of claims 1 to 9, wherein the polyol component comprises a mixture of polyether polyol and unsaturated polybutadiene polyol in a weight ratio from 90:10 to 40:60.
11. The thermoplastic polyurethane of claim 10, wherein the polyol component comprises a mixture of polyether polyol and unsaturated polybutadiene polyol in a weight ratio from 80:20 to 60:40.
12. The thermoplastic polyurethane of any of claims 1 to 11, wherein the polyether polyol has a number average molecular weight of 500 to 3000 measured by assay of terminal functional groups.
13. The thermoplastic polyurethane of claim 12, wherein the polyether polyol has a molecular weight of 1000 to 2500, measured by assay of terminal functional groups.
14. The thermoplastic polyurethane of any of claims 1 to 13, wherein the diisocyanate component comprises or consists of an aromatic diisocyanate.
15. The thermoplastic polyurethane of any of claims 1 to 14, wherein the diisocyanate component comprises or consists of 4,4'-methylenebis(phenyl isocyanate).
16. The thermoplastic polyurethane of any of claims 1 to 15, wherein the polybutadiene polyol comprises or consists of polybutadiene diol.
17. The thermoplastic polyurethane of any of claims 1 to 16, wherein the polyether polyol comprises poly(tetramethylene ether glycol).

18. The thermoplastic polyurethane of any of claims 1 to 17, wherein the polyether polyol component comprises a mixture of poly(tetramethylene ether glycol) and ethylene oxide end capped poly(propylene glycol).
19. The thermoplastic polyurethane of any of claims 1 to 16, wherein the polyether polyol comprises polypropylene glycol.
20. A thermoplastic polyurethane comprising the reaction product of:
- (a) a polyol component comprising a mixture of a polyether polyol and a polybutadiene polyol, wherein the polyether polyol is at least 50% by weight of the polyol component and wherein the polyether polyol comprises or consists of poly(tetramethylene ether glycol); and
 - (b) a diisocyanate component.
21. The thermoplastic polyurethane of claim 20, further comprising:
- (c) a chain extender component.
22. The thermoplastic polyurethane of claim 20 or 21, wherein the thermoplastic polyurethane has a hard segment content of 49% to 80% by weight or 54% to 75% by weight, wherein the hard segment content is defined as the combined weight of the diisocyanate component and the chain extender component.
23. The thermoplastic polyurethane of claim 21 or 22, wherein the chain extender component is selected from 1,4-butanediol, 2-butyl-2-ethyl-1,3-propandiol, dipropylene glycol, neopentyl glycol, or mixtures thereof.
24. The thermoplastic polyurethane of any of claims 20 to 23, wherein the polyether polyol consists of poly(tetramethylene ether glycol).
25. The thermoplastic polyurethane of any of claims 20 to 23, wherein the polyether polyol comprises or consists of a mixture of poly(tetramethylene ether glycol) and ethylene oxide end capped poly(propylene glycol).

26. The thermoplastic polyurethane of claim any of claims 20 to 25, wherein the polybutadiene polyol comprises or consists of polybutadiene diol.
27. The thermoplastic polyurethane of any of claims 20 to 26, wherein the polyol component comprises a mixture of the polyether polyol and polybutadiene diol in a weight ratio from 90:10 to 60:40 or 80:20 to 60:40.
28. The thermoplastic polyurethane of any of claims 20 to 27, wherein the polybutadiene diol is unsaturated.
29. The thermoplastic polyurethane of any of claims 20 to 28, wherein the diisocyanate component comprises or consists of an aromatic diisocyanate.
30. The thermoplastic polyurethane of claim 29, wherein the diisocyanate component comprises or consists of 4,4'-methylenebis(phenyl isocyanate).
31. An article made from the thermoplastic polyurethane composition of any of claims 1 to 30.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2020/050037

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G18/76 C08G18/66 C08G18/48 C08G18/62 C09D175/04
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
C08G C09D
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	WO 98/56841 A1 (STOWE WOODWARD COMPANY [US]; YANG YAN [US]) 17 December 1998 (1998-12-17) page 5, line 29 - page 6, line 6; claims 1-21; table 1 -----	1-6, 8-22, 24-31
X	US 2019/256641 A1 (FAUST RUDOLF [US]) 22 August 2019 (2019-08-22) paragraph [0040]; claims 1-18; examples 1-3 -----	1-31
Y	-----	1-31
Y	WO 2016/098073 A2 (STRAIT ACCESS TECHNOLOGIES HOLDINGS PTY LTD [ZA]) 23 June 2016 (2016-06-23) page 3, lines 3-11 page 5, lines 18-29 -----	1-31
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Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"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</p> <p>"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</p> <p>"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</p> <p>"&" document member of the same patent family</p>
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Date of the actual completion of the international search 10 November 2020	Date of mailing of the international search report 19/11/2020
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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 Scheuer, Sylvie
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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2020/050037

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2019/055342 A1 (NAM SANG CHUL [KR] ET AL) 21 February 2019 (2019-02-21) paragraph [0095]; examples 4-6 -----	1-31

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/US2020/050037

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9856841	A1	17-12-1998	AT 232886 T 15-03-2003
		AU 7832398 A 30-12-1998	
		CA 2281219 A1 17-12-1998	
		DE 69811493 T2 24-12-2003	
		EP 0988332 A1 29-03-2000	
		US 5994466 A 30-11-1999	
		WO 9856841 A1 17-12-1998	
US 2019256641	A1	22-08-2019	EP 3545040 A1 02-10-2019
			US 2019256641 A1 22-08-2019
			WO 2018057488 A1 29-03-2018
WO 2016098073	A2	23-06-2016	BR 112017013153 A2 02-01-2018
			CN 107531872 A 02-01-2018
			EP 3233954 A2 25-10-2017
			RU 2017125527 A 21-01-2019
			US 2018016380 A1 18-01-2018
			WO 2016098073 A2 23-06-2016
US 2019055342	A1	21-02-2019	CN 107614615 A 19-01-2018
			KR 101726700 B1 13-04-2017
			US 2019055342 A1 21-02-2019
			WO 2017195934 A1 16-11-2017