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(54) **Title:** POLYESTER POLYOL-POLYETHER POLYOL BLEND HAVING HIGHER STABILITY AND COMPARIBILITY, AND POLYURETHANE MATERIAL PREPARED THEREFROM

(57) **Abstract:** A polyester polyol/polyether polyol blend comprising a polyether polyol and a polyester polyol derived from multifunctional carboxylic acids and monoethylene glycol is provided, wherein the blend exhibits improved compatibility and stability, thus the polyurethane material prepared with the polyester polyol/polyether polyol blend can achieve high physical strengths, excellent dynamic properties and superior appearance.

POLYESTER POLYOL-POLYETHER POLYOL BLEND HAVING HIGHER STABILITY AND COMPARIBILITY, AND POLYURETHANE MATERIAL PREPARED THEREFROM

FIELD OF THE INVENTION

The present disclosure relates to a blend of polyester polyol and polyether polyol having improved stability and compatibility, a polyurethane prepared by using the same, and a method for improving the compatibility between polyester and polyether. The polyurethane material prepared with the polyester polyol-polyether polyol blend of the present disclosure exhibits high physical strengths, excellent dynamic properties and superior appearance.

BACKGROUND TECHNOLOGY

Over the past decades, polyurethane products have been employed in a wide range of end use applications such as footwear, solid tire, NVH (Noise, Vibration and Harshness) parts in automotive, polyurethane dispersions (PUD), composites and adhesives and the like. Molded polyurethane products are usually fabricated via a two-component process comprising the steps of reacting a first component mainly comprising polyols and optional additives such as foaming agents, catalysts, surfactants, etc. with a second component which comprises one or more prepolymers obtained by reacting polyols with isocyanate compounds having at least two free isocyanate groups. The two components are blended at high speed and then transferred into varied molds with desired shapes.

Polyether polyol/polyester polyol hybrid systems are often used as polyol component in these polyurethane applications to combine both property benefits from polyester and polyether polyol based systems. These property benefits include improved toughness and wear-resistance derived from polyester polyols and hydrolysis-resistance, microbial attack resistance as well as low viscosity derived from polyether polyols. However, the problem is that polyester and polyether polyols are not compatible to each other and will sendiment with increasing time if blended together to form polyol components, leading to processing and quality issues in the industry. Two technical means has been adopted to overcome the incompatibility issue between polyester and polyether polyols. One means is to collect all the polyether polyols together to form a stable polyol component, whereas all the polyester

polyols react with isocyantes to form the prepolymer component having free isocyantae groups. These two components, although inherently incompatible, then reacted under high speed mixing to form a polyurethane product. However, due to the inherent incompatibility between the polyether polyol and polyester polyol, the resultant polyurethane product exhibits deteriorated physical strengths such as tear strength, abrasion-resistance and etc. as well as dynamic properties. The another approach is to copolymerize polyester polyol and polyether polyol together, in which case, ester and ether moieties are chemically conjugated together to form macromoleulcar chains so that incompatibility of the two moieties is improved in the molecular level. However, this approach will incur additional process complexity and cost and thus will not be actually commercialized. Besides, such an approach still cannot achieve desirable advantages.

For the above reasons, there is still a need in the polyurethane manufacture industry to develop a technology which can overcome the incompatibility issue in a cost-effective way, and can produce a polyurethane composition whose performance properties as stated above can be improved with an economical way. After persistent exploration, the inventors have surprisingly developed a polyether-polyester polyol blend which can achieve one or more of the above targets.

SUMMARY OF THE INVENTION

The present disclosure provides a unique polyether-polyester polyol blend, a polyurethane composition, a polyurethane material and a molded product prepared by using the same, a method for preparing the polyurethane material and a method for improving the compatibility between the polyether polyol and the polyester polyol.

In a first aspect of the present disclosure, the present disclosure provides a polyol composition comprising:

(A) a first polyester polyol derived from (i) at least one C_2-C_{20} multifunctional carboxylic acid, anhydride thereof, derivative thereof, or a blend thereof, and (ii) at least one aliphatic polyol compound;

(B) at least one first polyether polyol;

wherein the aliphatic polyol compound comprises at least 50wt% of monoethylene glycol, based on the total weight of the aliphatic polyol compound; and

wherein the first polyester polyol and the first polyether polyol are not covalently bonded.

According to a preferable embodiment of the present disclosure, the aliphatic polyol compound comprises 50wt% of monoethylene glycol and up to 50wt% of at least one co-polyol compound, based on the total weight of the aliphatic polyol compound, and

wherein the co-polyol compound is selected from a group consisting to a C_3-C_{20} aliphatic multifunctional alcohol, C_3-C_{20} alicyclic multifunctional alcohol, C_7-C_{20} aromatic multifunctional alcohol, dimer thereof, trimer thereof, and a blend thereof.

According to another preferable embodiment of the present disclosure, the aliphatic polyol compound comprises 100wt% of monoethylene glycol, based on the total weight of the aliphatic polyol compound. In other words, the polyols used for preparing the first polyester polyol exclusively comprise the monoethylene glycol and does not comprise any other polyols.

According to another preferable embodiment of the present disclosure, the first polyether polyol is derived from a polycondensation reaction of at least one raw material selected from the group consisting of C_2-C_{10} alkylene oxide, C_2-C_{12} alkylene glycol, C_2-C_{10} aliphatic triol, C_2-C_{10} aliphatic tetraol, and a blend thereof.

In a second aspect of the present disclosure, the present disclosure provides a polyurethane composition, comprising

(I) an isocyanate component comprising at least one prepolymer having at least two free isocyanate groups, wherein the prepolymer is prepared by reacting a first isocyanate compound having at least two free isocyante groups with at least one first isocyanate-reactive compound; and

(II) an isocyanate-reactive component;

wherein at least one of the first isocyanate-reactive compound and the isocyanate-reactive component comprises the first polyester polyol of the present disclosure or the polyol composition of the present disclosure.

According to another preferable embodiment of the present disclosure, at least one of the first isocyanate-reactive compound and the isocyanate-reactive component comprises a second polyol compound selected from the group consisting of a C_2-C_{16} aliphatic polyhydric alcohol comprising at least two hydroxyl groups, a C_6-C_{15} cycloaliphatic or aromatic polyhydric alcohol comprising at least two hydroxyl groups, a C_7-C_{15} araliphatic polyhydric

alcohol comprising at least two hydroxyl groups, a polyester polyol which is different from the first polyester polyol and has a molecular weight from 100 to 5,000 and an average hydroxyl functionality of 1.5 to 5.0, a polyether which is different from the first polyether polyol, and combinations thereof.

According to another preferable embodiment of the present disclosure, the isocyanate component optionally further comprises at least one second monomeric isocyanate compound having at least two free isocyante groups, and wherein the first isocyanate compound and the second monomeric isocyanate compound are separately selected from the group consisting of C_2-C_{12} aliphatic polyisocyanate comprising at least two isocyanate groups, C_6-C_{15} cycloaliphatic or aromatic polyisocyanate comprising at least two isocyanate groups, C_7-C_{15} araliphatic polyisocyanate comprising at least two isocyanate groups, and any combinations thereof.

In a third aspect of the present disclosure, the present disclosure provides a method for preparing a polyurethane material with the polyurethane composition according to the present disclosure, comprising a step of combining (I) the isocyanate component with (II) the isocyanate-reactive component.

In a fourth aspect of the present disclosure, the present disclosure provides a polyurethane material prepared with the above said method.

In a fifth aspect of the present disclosure, the present disclosure provides a method for enhancing the compatibility between a polyester and a polyether, comprising:

(a) reacting at least one C_2-C_{20} multifunctional carboxylic acid, anhydride thereof, or a blend thereof with at least one aliphatic polyol compound to form a first polyester polyol, wherein the aliphatic polyol compound comprises at least 50wt%, preferably from 50 to 100wt%, more preferably 100wt% of monoethylene glycol, based on the total weight of the aliphatic polyol compound;

(b) providing at least one first polyether polyol; and

(c) physically blending the first polyester polyol with the first polyether polyol;

wherein the first polyester polyol and the first polyether polyol are not covalently bonded.

It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the invention,

as claimed.

DETAILED DESCRIPTION OF THE INVENTION

Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which the invention belongs. Also, all publications, patent applications, patents, and other references mentioned herein are incorporated by reference.

As disclosed herein, "and/or" means "and, or as an alternative". All ranges include endpoints unless otherwise indicated. Unless indicated otherwise, all the percentages and ratios are calculated based on weight, and all the molecular weights are number average molecular weights.

The present disclosure has surprisingly developed a technology for notably improve the compatibility and miscibility between the polyester polyol and polyether polyol. In particular, it is found that monoethylene glycol (MEG)-based low viscosity polyester polyols has good compatibility with the polyether polyols. Such a technical breakthrough is completely unpredictable according to the existing theoretical and experimental research results since MEG is the shortest dialcohol blocks and thus polyester polyols based on MEG contain the most amount of ester bonds under the same molecular weight. The high ester bond density will cause significant interchain interaction between macromolecular polyester polyols, leading to increment of viscosity. Besides, the high ester bond density should also impart more polarity to the polyester polyols, leading to higher incompatibility with polyether polyols. In other words, a person skilled in the art will be hindered by a prejudice that a polyester polyol prepared with MEG shall be the most incompatible with polyether polyol and has no motivation to prepare a polyester/polyether polyol blend by using MEG as a raw material for the preparation of polyester polyol. However, it is surprisingly found in this disclosure that the disclosed polyester polyols based on MEG has a quite low viscosity and can be blended with polyether polyols and form a stable and homogenous polyol composition/component for a later application, such as preparation of polyurethane, preparation of isocyanate prepolymer, and any other applications which may benefit from a stable polyester polyol/polyether polyol blend.

In the context of the present disclosure, the polyester polyol which exhibits improved compatibility/miscibility with polyether polyol is known as “the first polyester polyol”, “the

inventive polyester polyol" or "the polyester polyol of the present disclosure". The polyether polyol which is combined with the first polyester polyol and forms a stable polyester polyol/polyether polyol blend is known as "the first polyether polyol".

According to various embodiments of the present disclosure, the polyol raw material used for preparing the first polyester polyol is at least one aliphatic polyol compound comprising at least 50wt% of monoethylene glycol, based on the total weight of the aliphatic polyol compound, preferably from 50 to 100wt%, or from 55 to 100wt%, or from 60 to 100wt%, or from 65 to 100wt%, or from 70 to 100wt%, or from 75 to 100wt%, or from 80 to 100wt%, or from 85 to 100wt%, or from 90 to 100wt%, or from 95 to 100wt%, or from 98 to 100wt%, monoethylene glycol. According to a most preferable embodiment of the present disclosure, all the aliphatic polyol compound used for preparing the first polyester polyol is exclusively monoethylene glycol, i.e. the aliphatic polyol compound does not comprise any polyol other than monoethylene glycol.

According to an alternative embodiment of the present disclosure, the first polyether polyol further comprises at least of a co-polyol compound which is different from monoethylene glycol and can be selected from the group consisting of a C_3-C_{20} aliphatic multifunctional alcohol, C_3-C_{20} alicyclic multifunctional alcohol, C_7-C_{20} aromatic multifunctional alcohol, dimer thereof, trimer thereof, and a blend thereof. Preferably, the co-polyol compound is selected from the group consisting of C_3-C_6 aliphatic diol and dimer thereof, such as diethylene glycol, 1,3-propane diol, 2-methyl-1,3-propane diol, 1,4-butane diol, 1,6-hexane diol, and a combination thereof. According to a preferable embodiment of the present disclosure, the amount of the co-polyol compound is up to 50 wt%, or up to 45 wt%, or up to 40 wt%, or up to 35 wt%, or up to 30 wt%, or up to 25 wt%, or up to 20 wt%, or up to 15 wt%, or up to 10 wt%, or up to 5 wt%, or up to 2 wt%, or up to 1 wt%, or 0wt%, based on the total weight of the aliphatic polyol compound.

According to various embodiments of the present disclosure, the carboxylic acid compounds used for preparing the first polyester polyol is at least one C_2-C_{20} multifunctional carboxylic acid, anhydride thereof, derivative thereof, or a blend thereof. In particular, the carboxylic acid compounds used for preparing the first polyester polyol can be aliphatic, cycloaliphatic, araliphatic, aromatic or heterocyclic dibasic carboxylic acids or polycarboxylic acids, or anhydrides/esters thereof, and may be substituted, for example with halogen atoms,

and/or may be saturated or unsaturated. Examples of said carboxylic acid includes adipic acid, adipic anhydride, suberic acid, azelaic acid, phthalic acid, isophthalic acid, phthalic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, tetrachlorophthalic anhydride, endomethylene-tetrahydro- phthalic anhydride, glutaric anhydride, alkenylsuccinic acid, maleic acid, maleic anhydride, fumaric acid, dimeric fatty acids. Preference is given to dicarboxylic acids represented the general formula HOOC-$(CH_2)_y$-COOH, where y is an integer from 1 to 20, preferably an integer of 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10. According to a preferable embodiment of the present disclosure, the carboxylic acid compounds used for preparing the first polyester polyol exclusively comprise one or more dicarboxylic acids represented the general formula HOOC-$(CH_2)_y$-COOH. According to a most preferable embodiment of the present disclosure, the carboxylic acid compounds used for preparing the first polyester polyol exclusively comprise adipic acid.

According to a preferable embodiment of the present disclosure, the first polyester polyol can be synthesized via a condensation polymerization reaction at a temperature of e.g. from ambient temperature to 300°C, such as from 80 to 280°C, or from 100 to 260°C, or from 120 to 250°C, or from 150 to 240°C, or from 180 to 240°C; for a duration of 0.5 to 20 hours, or from 1 to 15 hours, or from 1.5 to 12 hours, or from 2 to 10 hours, or from 3 to 8 hours, or from 4 to 7 hours, or from 5 to 6 hours. The condensation polymerization reaction can be conducted in the presence of an esterification catalyst selected from the group consisting of p-toluenesulfonic acid; titannium (IV) based catalysts such as such as tetraisopropyl titanate, tetra(n-butyl) titanate, tetraoctyl titanate, titanium acetic acid salts, titanium diisopropoxybis(acetylacetonate), and titanium diisopropoxybis (ethyl acetoacetate); zirconium-based catalysts such as zirconium tetraacetylacetonate, zirconium hexafluoroacetylacetonate, zirconium trifluoroacetylacetonate, tetrakis (ethyltrifluoroacetyl-acetonate) zirconium, tetrakis(2,2,6,6-tetramethyl-heptanedionate), zirconium dibutoxybis (ethylacetoacetate), and zirconium diisopropoxybis (2, 2, 6, 6-tetramethyl-heptanedionate); and tin (II) and tin (IV)-based catalysts such as tin diacetate, tin dioctanoate, tin diethylhexanoate, tin dilaurate, dibutyltin diacetate, dibutyltin dilaurate, dibutyltin maleate, dioctyltin diacetate, dimethyltin dineodecanoate, dimethylhydroxy (oleate) tin, and dioctyldilauryltin; and bismuth-based catalyst such as bismuth octanoate.

According to an embodiment of the present disclosure, the molar ratio between the

carboxylic group in the carboxylic acid compounds and the hydroxyl group in the aliphatic polyol compound, which comprises both monoethylene glycol and optional co-polyol compound, is from 100:50 to 50:100, preferably from 100:70 to 70:100, more preferably from 100:90 to 90:100, or from 100:99 to 99:100, or at around 100:100, and the resultant first polyester polyol has a hydroxyl functionality (average number of free hydroxyl group per molecule) of 1.0 to 4.0, or from 1.1 to 3.8, or from 1.2 to 3.5, or from 1.5 to 3.0, or from 1.8 to 2.8, or from 2.0 to 2.5, or from 2.2 to 2.4. According to another embodiment of the present disclosure, the first polyester polyol has a molecular weight of 200 to 6,000 g/mol, such as from 400 to 5,500 g/mol, or from 500 to 5,000 g/mol, or from 600 to 4,500 g/mol, or from 700 to 4,000 g/mol, or from 800 to 3,500 g/mol, or from 1,000 to 3,000 g/mol, or from 1,200 to 2,500 g/mol, or from 1,500 to 2,200 g/mol, or from 1,800 to 2,000 g/mol.

According to various embodiments of the present disclosure, the first polyester polyol (having different amount of repeating units derived from MEG) can be physically blended with a first polyether polyol to form a stable and homogeneous blend. The first polyether polyol can be derived from a polycondensation reaction of at least one raw material selected from the group consisting of C_2-C_{10} alkylene oxide, C_2-C_{12} alkylene glycol, C_2-C_{10} aliphatic triol, C_2-C_{10} aliphatic tetraol, and a blend thereof.

According to an embodiment of the present disclosure, the first polyether polyol to be combined with the first polyester polyol has a molecular weight of 100 to 8,000 g/mol, and may have a molecular weight in the numerical range obtained by combining any two of the following end point values: 120, 150, 180, 200, 250, 300, 350, 400, 450, 500, 550, 600, 700, 800, 900, 1000, 1100, 1200, 1300, 1400, 1500, 1600, 1700, 1800, 1900, 2000, 2100, 2200, 2300, 2400, 2500, 2600, 2700, 2800, 2900, 3000, 3100, 3200, 3300, 3400, 3500, 3600, 3700, 3800, 3900, 4000, 4100, 4200, 4300, 4400, 4500, 4600, 4700, 4800, 4900, 5000, 5200, 5400, 5600, 5800, 6000, 6200, 6400, 6500, 6800, 7000, 7200, 7400, 7500, 7600, 7800, 8000 g/mol.

In various embodiments, the first polyether polyol to be combined with the first polyester polyol has an average hydroxyl functionality of 1.5 to 5.0, and may have an average hydroxyl functionality in the numerical range obtained by combining any two of the following end point values: 1.6, 1.7, 1.8, 1.9, 2.0, 2.1, 2.2, 2.3, 2.4, 2.5, 2.6, 2.7, 2.8, 2.9, 3.0, 3.1, 3.2, 3.3, 3.4, 3.5, 3.6, 3.7, 3.8, 3.9, 4.0, 4.1, 4.2, 4.3, 4.4, 4.5, 4.6, 4.7, 4.8, 4.9 and 5.0. According to a preferable embodiment of the present disclosure, the first polyether polyol can be selected

from the group consisting of polyethylene glycol, polypropylene glycol, polytetramethylene glycol, poly(2-methyl-1,3-propane glycol) and any copolymers thereof, such as poly(ethylene oxide-propylene oxide) glycol.

According to an embodiment of the present disclosure, the polyether polyols can be prepared by polymerization of one or more linear or cyclic alkylene oxides selected from propylene oxide (PO), ethylene oxide (EO), butylene oxide, tetrahyfrofuran, 2-methyl-1,3-propane glycol and mixtures thereof, with proper starter molecules in the presence of a catalyst. Typical starter molecules include compounds having at least 1, preferably from 1.5 to 3.0 hydroxyl groups or having one or more primary amine groups in the molecule. Suitable starter molecules having at least 1 and preferably from 1.5 to 3.0 hydroxyl groups in the molecules are for example selected from the group comprising ethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butenediol, 1,4-butynediol, 1,5-pentanediol, neopentyl glycol, 1,4-bis(hydroxymethyl) -cyclohexane, 1,2-bis(hydroxymethyl)cyclohexane, 1,3-bis(hydroxymethyl) -cyclohexane, 2-methylpropane-1,3-diol, methylpentanediols, diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycol, dipropylene glycol, polypropylene glycol, dibutylene glycol, polybutylene glycols, trimethylolpropane, glycerol, pentaerythritol, castor oil, sugar compounds such as, for example, glucose, sorbitol, mannitol and sucrose, polyhydric phenols, resols, such as oligomeric condensation products of phenol and formaldehyde and Mannich condensates of phenols, formaldehyde and dialkanolamines, and also melamine. Starter molecules having one or more primary amine groups in the molecules may be selected for example from the group consisting of aniline, EDA, TDA, MDA and PMDA, more preferably from the group comprising TDA and PMDA, an most preferably TDA. When TDA is used, all isomers can be used alone or in any desired mixtures. For example, 2,4-TDA, 2,6-TDA, mixtures of 2,4-TDA and 2,6-TDA, 2,3-TDA, 3,4-TDA, mixtures of 3,4-TDA and 2,3-TDA, and also mixtures of all the above isomers can be used. Catalysts for the preparation of polyether polyols may include alkaline catalysts, such as potassium hydroxide, for anionic polymerization or Lewis acid catalysts, such as boron trifluoride, for cationic polymerization. Suitable polymerization catalysts may include potassium hydroxide, cesium hydroxide, boron trifluoride, or a double cyanide complex (DMC) catalyst such as zinc hexacyanocobaltate or quaternary phosphazenium compound. In a preferable embodiment of the present disclosure, the starting material polyether polyol

includes polyethylene, (methoxy)polyethylene glycol (MPEG), polyethylene glycol (PEG), poly(propylene glycol), polytetramethylene glycol, poly(2-methyl-1,3-propane glycol) or copolymer of ethylene epoxide and propylene epoxide (polyethylene glycol-propylene glycol) with primary hydroxyl ended group or secondary hydroxyl ended group.

According to a preferable embodiment of the present disclosure, the weight ratio between the first polyester polyol and the first polyether polyol is from 1:99 to 99:1, or from 10:90 to 90:10, or from 15:85 to 85:15, or from 20:80 to 80:20, or from 25:75 to 75:25, or from 30:70 to 70:30, or from 35:65 to 65:35, or from 40:60 to 60:40, or from 45:55 to 55:45, or at about 50:50.

According to a preferable embodiment of the present disclosure, the stable and homogeneous blend of a first polyester polyol and a first polyether polyol, i.e. the polyol composition of the present disclosure, is used for the preparation of polyurethane material. For example, the polyol composition of the present disclosure can be used in the isocyanate-reactive component (II) of the polyurethane composition, or/and can be used for preparing the prepolymer of the isocyanate component (I).

According to an embodiment of the present disclosure, the isocyanate-reactive component (II) of the polyurethane composition comprises the polyol composition of the present disclosure (i.e. the stable and homogeneous blend of a first polyester polyol and a first polyether polyol). According to another embodiment of the present disclosure, all the polyols in the isocyanate-reactive component (II) of the polyurethane composition exclusively comprise the polyol composition of the present disclosure (i.e. the stable and homogeneous blend of a first polyester polyol and a first polyether polyol), and do not comprise any other polyols.

According to an embodiment of the present disclosure, the polyol used for preparing the prepolymer of the isocyanate component (I) of the polyurethane composition comprises the polyol composition of the present disclosure (i.e. the stable and homogeneous blend of a first polyester polyol and a first polyether polyol). According to another embodiment of the present disclosure, all the polyols used for preparing the prepolymer of the isocyanate component (I) of the polyurethane composition exclusively comprise the polyol composition of the present disclosure (i.e. the stable and homogeneous blend of a first polyester polyol and a first polyether polyol), and do not comprise any other polyols.

According to an embodiment of the present disclosure, the isocyanate-reactive component (II) of the polyurethane composition comprises the first polyester polyol. According to another embodiment of the present disclosure, all the polyols in the isocyanate-reactive component (II) of the polyurethane composition exclusively comprise the first polyester polyol, and do not comprise any other polyols.

According to an embodiment of the present disclosure, the polyol used for preparing the prepolymer of the isocyanate component (I) of the polyurethane composition comprises the first polyester polyol. According to another embodiment of the present disclosure, all the polyols used for preparing the prepolymer of the isocyanate component (I) of the polyurethane composition exclusively comprise the first polyester polyol, and do not comprise any other polyols.

Various combinations of all the embodiments of the present disclosure are also within the technical concept of the present disclosure.

In the following paragraphs, the advantageous performance properties derived from the stable and homogeneous polyester polyol and polyether polyol blend are characterized and described in a polyurethane system, but it shall be understood that the stable and homogeneous polyester polyol and polyether polyol blend of the present disclosure can be effectively in an applications which may benefit from the improved compatibility between polyester polyol and polyether polyol.

According to an embodiment of the present disclosure, the polyurethane composition can be a "two-component", "two-part" or "two-package" composition comprising at least one isocyanate component (A) and an isocyanate-reactive component (B), wherein the isocyanate component (A) preferably comprises a prepolymer comprising at least two free isocyanate groups and is prepared by reacting at least one polyisocyanate compound with at least one first isocyanate-reactive compound. The isocyanate component (A) and the isocyanate-reactive component (B) are transported and stored separately, combined shortly or immediately before being applied during the manufacture of the polyurethane product, such as solid tire. Once combined, the isocyanate groups in component (A) reacts with the isocyanate-reactive groups (particularly, hydroxyl group) in component (B) to form polyurethane.

Without being limited to any specific theory, it is believed that the first polyester polyol at least partially derived from MEG exhibits unexpected low viscosity and good

compatibility with polyether polyol, wherein the low viscosity is beneficial for material handling and processing, and the good compatibility with polyether polyol imparts the resultant polyurethanes with excellent physical strengths, superior dynamic properties and good part appearance.

In various embodiments, the isocyanate compound used for the isocyanate component (I), such as those used for preparing the prepolymer or used in combination with the prepolymer, may include an aliphatic, cycloaliphatic, aromatic or heteroaryl compound having at least two isocyanate groups. In a preferable embodiment, the isocyanate compound can be selected from the group consisting of C_4-C_{12} aliphatic polyisocyanates comprising at least two isocyanate groups, C_6-C_{15} cycloaliphatic or aromatic polyisocyanates comprising at least two isocyanate groups, C_7-C_{15} araliphatic polyisocyanates comprising at least two isocyanate groups, and combinations thereof. In another preferable embodiment, suitable polyisocyanate compounds include m-phenylene diisocyanate, 2,4-toluene diisocyanate and/or 2,6-toluene diisocyanate (TDI), the various isomers of diphenylmethanediisocyanate (MDI), carbodiimide modified MDI products, hexamethylene-1,6-diisocyanate, tetramethylene-1,4-diisocyanate, cyclohexane-1,4-diisocyanate, hexahydrotoluene diisocyanate, hydrogenated MDI, naphthylene-1,5-diisocyanate, isophorone diisocyanate (IPDI), or mixtures thereof. Generally, the amount of the isocyanate compound may vary based on the actual requirement of the polyurethane foam and the polyurethane tire. For example, as one illustrative embodiment, the content of the isocyanate compound can be from 15 wt% to 60 wt%, or from 20 wt% to 50 wt%, or from 23 wt% to 40 wt%, or from 25 wt% to 35 wt%, based on the total weight of the polyurethane composition. According to a preferable embodiment of the present disclosure, the amount of the isocyanate compound is properly selected so that the isocyanate group is present at a stoichiometric molar amount relative to the total molar amount of the hydroxyl groups included in the isocyanate component, the isocyanate-reactive component, and any additional additives or modifiers.

Additionally or alternatively, the polyol used for preparing the prepolymer of the isocyanate component (I) and the isocyanate-reactive component may comprise a polyol other than the stable polyester polyol/polyether polyol blend of the present disclosure, or may comprise a polyol other than the first polyester polyol at least partially derived from the MEG (hereinafter referred as “second polyol compound” for short).

According to various embodiments of the present disclosure, the second polyol compound can be selected from the group consisting of C_2-C_{16} aliphatic polyhydric alcohols comprising at least two hydroxyl groups, C_6-C_{15} cycloaliphatic or aromatic polyhydric alcohols comprising at least two hydroxyl groups, C_7-C_{15} araliphatic polyhydric alcohols comprising at least two hydroxyl groups, a second polyester polyol which is different from the first polyester polyol and has a molecular weight from 100 to 5,000 and an average hydroxyl functionality of 1.5 to 5.0, a second polyether polyol which is different from the first polyether polyol and may have a molecular weight of e.g. from 100 to 5,000 and an average hydroxyl functionality of 1.5 to 5.0, and combinations thereof.

The isocyanate prepolymer prepared by reacting the first isocyanate compound with the first isocyanate-reactive compound has a NCO group content of from 5 to 60 wt%, preferably from 6 to 49 wt%, based on the total weight of the prepolymer.

The reaction between the first isocyanate compound and the first isocyanate-reactive compound, and the reaction between the prepolymer and the isocyanate-reactive component may occur in the presence of one or more catalysts that can promote the reaction between the isocyanate group and the hydroxyl group. Without being limited to theory, the catalysts can include, for example, glycine salts; tertiary amines; tertiary phosphines, such as trialkylphosphines and dialkylbenzylphosphines; morpholine derivatives; piperazine derivatives; chelates of various metals, such as those which can be obtained from acetylacetone, benzoylacetone, trifluoroacetyl acetone, ethyl acetoacetate and the like with metals such as Be, Mg, Zn, Cd, Pd, Ti, Zr, Sn, As, Bi, Cr, Mo, Mn, Fe, Co and Ni; acidic metal salts of strong acids such as ferric chloride and stannic chloride; salts of organic acids with variety of metals, such as alkali metals, alkaline earth metals, Al, Sn, Pb, Mn, Co, Ni and Cu; organotin compounds, such as tin(II) salts of organic carboxylic acids, e.g., tin(II) diacetate, tin(II) dioctanoate, tin(II) diethylhexanoate, and tin(II) dilaurate, and dialkyltin(IV) salts of organic carboxylic acids, e.g., dibutyltin diacetate, dibutyltin dilaurate, dibutyltin maleate and dioctyltin diacetate; bismuth salts of organic carboxylic acids, e.g., bismuth octanoate; organometallic derivatives of trivalent and pentavalent As, Sb and Bi and metal carbonyls of iron and cobalt; or mixtures thereof.

Tertiary amine catalysts include organic compounds that contain at least one tertiary nitrogen atom and are capable of catalyzing the hydroxyl/isocyanate reaction. The tertiary

amine, morpholine derivative and piperazine derivative catalysts can include, by way of example and not limitation, triethylenediamine, tetramethylethylenediamine, pentamethyl-diethylene triamine, bis(2-dimethylaminoethyl)ether, triethylamine, tripropylamine, tributyl-amine, triamylamine, pyridine, quinoline, dimethylpiperazine, piperazine, N-ethylmorpholine, 2-methylpropanediamine, methyltriethylenediamine, 2,4,6-tridimethylamino-methyl)phenol, N,N',N"-tris(dimethyl amino-propyl)sym-hexahydro triazine, or mixtures thereof.

In general, the content of the catalyst used herein is larger than zero and is at most 3.0 wt%, preferably at most 2.5 wt%, more preferably at most 2.0 wt%, based on the total weight of the polyurethane composition.

In various embodiments of the present disclosure, the polyurethane composition comprises one or more additives selected from the group consisting of chain extenders, crosslinkers, blowing agents, foam stabilizers, tackifiers, plasticizers, rheology modifiers, antioxidants, fillers, colorants, pigments, water scavengers, surfactants, solvents, diluents, flame retardants, slippery-resistance agents, antistatic agents, preservatives, biocides, antioxidants and combinations of two or more thereof. These additives can be transmitted and stored as independent components and incorporated into the polyurethane composition shortly or immediately before the combination of components (A) and (B). Alternatively, these additives may be contained in either of components (A) and (B) when they are chemically inert to the isocyanate group or the isocyanate-reactive group.

A chain extender may be present in the reactants that form the polyurethane material. A chain extender is a chemical having two isocyanate-reactive groups per molecule and an equivalent weight per isocyanate-reactive group of less than 300, preferably less than 200 and especially from 31 to 125. The isocyanate reactive groups are preferably hydroxyl, primary aliphatic or aromatic amino or secondary aliphatic or aromatic amino groups. Representative chain extenders include ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propylene glycol, dipropylene glycol, tripropylene glycol, 1,4-butanediol, cyclohexane dimethanol, ethylene diamine, phenylene diamine, bis(3-chloro-4-aminophenyl)methane, dimethylthio-toluenediamine and diethyltoluenediamine.

One or more crosslinkers also may be present in the reactants that form the polyurethane material. For purposes of this invention, "crosslinkers" are materials having three or more isocyanate-reactive groups per molecule and an equivalent weight per isocyanate-

reactive group of less than 300. Crosslinkers preferably contain from 3 to 8, especially from 3 to 4 hydroxyl, primary amine or secondary amine groups per molecule and have an equivalent weight of from 30 to about 200, especially from 50 to 125. Examples of suitable crosslinkers include diethanol amine, monoethanol amine, triethanol amine, mono-, di- or tri(isopropanol) amine, glycerine, trimethylol propane, pentaerythritol, and the like.

Chain extenders and crosslinkers are suitably used in small amounts, as hardness increases as the amount of either of these materials increases. From 0 to 25 parts by weight, or from 0.1 to 25 parts by weight of a chain extender is suitably used per 100 parts by weight of the polyol component. A preferred amount is from 1 to 15 parts per 100 parts by weight of the polyol component. From 0 to 10 parts by weight of a crosslinker is suitably used per 100 parts by weight of the polyol component. A preferred amount is from 0 to 5 parts per 100 parts by weight of the polyol component.

A filler may be present in the polyurethane composition. Fillers are mainly included to reduce cost. Particulate rubbery materials are especially useful fillers. Such a filler may constitute from 1 to 50% or more of the weight of the polyurethane composition.

Suitable blowing agents include water, air, nitrogen, argon, carbon dioxide, hydrocarbons, hydrofluorocarbons, hydrochlorofluorocarbons and other volatile chemicals with low boiling points of from -30 ^{o}C to 75^{o}C.

A surfactant may be present in the reaction mixture. It can be used, for example, if a cellular tire filling is desired, as the surfactant stabilizes a foaming reaction mixture until it can harden to form a cellular polymer. A surfactant also may be useful to wet filler particles and thereby help disperse them into the reactive composition and the elastomer. Silicone surfactants are widely used for this purpose and can be used here as well. The amount of surfactant used will in general be between 0.02 and 1 part by weight per 100 parts by weight polyol component.

According to a preferable embodiment of the present disclosure, one or more foam stabilizer, such as silicone-based foam stabilizers; anti-foam agents, such as silicone-based anti-foam agents; functional additives, such as anti-static electricity agents, flame-retardant agents, slippery resistance agents, and etc. may be further included in the polyurethane composition.

According to a preferable embodiment of the present disclosure, the stable and

compatible polyester polyol/polyether polyol blend of the present application is suitable for preparing a polyurethane product, especially a polyurethane tire, such as a solid tire. Preferably, the invention is applicable to prepare a material for a wide range of tires that can be used in many applications. The tires can be, for example, for a bicycle, a cart such as a golf cart or shopping cart, a motorized or unmotorized wheelchair, an automobile or truck, any other type of transportation vehicles including an aircraft, as well as various types of agriculture, industrial and construction equipment. Large tires that have an internal volume of 0.1 cubic meter or more are of particular interest.

According to various embodiments of the present disclosure, the polyurethane material has a density of at least 100 kg/m^3, such as from 100 to 950 kg/m^3, from 200 to 850 kg/m^3, from 300 to 800 kg/m^3, from 400 to 750 kg/m^3, from 500 to 700 kg/m^3, from 550 to 650 kg/m^3, or from 580 to 620 kg/m^3, or about 600 kg/m^3.

According a preferable embodiment of the present disclosure, the polyurethane composition is substantially free of water or moisture intentionally added therein. For example, "free of water" or "water free" means that the mixture of all the raw materials used for preparing the polyurethane composition comprise less than 3% by weight, preferably less than 2% by weight, preferably less than 1% by weight, more preferably less than 0.5% by weight, more preferably less than 0.2% by weight, more preferably less than 0.1% by weight, more preferably less than 100 ppm by weight, more preferably less than 50 ppm by weight, more preferably less than 10 ppm by weight, more preferably less than 1ppm by weight of water, based on the total weight of the mixture of raw materials.

EXAMPLES

Some embodiments of the invention will now be described in the following Examples. However, the scope of the present disclosure is not, of course, limited to the formulations set forth in these examples. Rather, the Examples are merely inventive of the disclosure.

The information of the raw materials used in the examples is listed in the following table 1:

Table 1. Raw materials used in the examples

Components	Grades	Suppliers
MDI	ISONATE™ M125	The Dow Chemical Company
Di-acid	Adipic acid (AA)	Shenma Inc.

Di-alcohol	Monoethylene glycol (MEG)	Shanghai Tony Trade Co., Ltd.
Esterification catalyst	n-Butyl titanate (TBT)	Merck Inc.
Carbodiimide-modified MDI	Isonate™ 143LP	The Dow Chemical Company
Carbodiimide-modified MDI	Isonate™ PR 7020	The Dow Chemical Company
Prepolymer comprising at least two free isocyanate groups	PTMEG 2000 Prepolymer, a prepolymer derived from MDI and Polytetramethylene ether glycol	Dongda Inov., China
Inhibitor	Benzoyl Chloride	Daejung, Korea
Polyether polyol	Voranol™ CP 6001	The Dow Chemical Company
Polymer polyol	SPECFLEX™ NC 701	The Dow Chemical Company
Chain extender	1,4-butane diol (BDO)	BASF
Polyether polyol	Polytetramethylene ether glycol (PTMEG) 2000	Dairen Chemical Corporate, Taiwan
Polybutadiene liquid polymer	LITHENE ULTRA N4-9000	Synthomer Inc.
Foam stabilizer	Tegostab B-8408	Evonik
Foam stabilizer	Dabco DC 193	Evonik
Strong blowing catalyst	Niax A-1, 70% bis(dimethylaminoethyl)ether and 30% DPG	Momentive
Balanced catalyst	Polycat 77, Bis(dimethylaminopropyl)methylamine	Evonik
Delayed catalyst, gelling and back cure	Dabco DC-1	Evonik
Gelling catalyst	Fomrez UL-38	Momentive
Dabco 33s	Dabco 33s, 33% TEDA diluted in 67% of 1,4-BDO	Evonik

1. Characterization Technologies

Viscosities of different polyols and prepolymers were determined using viscosity analyzer (CAP, Brookfield) at various temperatures. Acid-value, hydroxyl-value and NCO value were determined according to ASTMD4662, ASTMD4274 and ASTM D5155, respectively. Tensile strength, elongation at break and tear strength were determined on a Gotech AI-7000S1 universal testing machine according to the testing method DIN 53543. Abrasion loss was determined on a Gotech GT-7012-D abrasion tester according to the testing method DIN 53516. Dynamic mechanical analysis (DMA) was performed on a TA RSA G2 analyzer under strain-control mode at a frequency of 1 Hz. Thermogravimetric analysis (TGA)

was conducted on a TA-Q500 analyzer in a temperature range from 0 °C to 600 °C in air atmosphere. Differential scanning calorimeter (DSC) was performed on a TA Q1500 analyzer with a cooling speed of 10 °C/min and heating speed of 20 °C/min under N_2 atmosphere.

2. Experiments

2.1 Inventive Examples 1-3 and Comparative Examples 1-2: Synthesis and characterization of polyester polyols

Three inventive polyester polyols (In.Ex.1-3) and two comparative polyester polyols (Com.Ex.1-2) were prepared via a condensation copolymerization reaction process by using the recipes shown in Table 2. For example, a general procedure for conducting these preparation examples is as follows: all the dicarboxylic acid and diol raw materials as shown in table 2 were fed all at once into a glass reactor equipped with a vacuum pump and oil bath under nitrogen atmosphere at room temperature. The content in the reactor was stirred all through the reaction. Firstly the reactants were heated up stepwise to a temperature of 180°C, kept at this temperature for 4 hours, then heated up to a temperature of 240°C, and was kept at this temperature until the acid value of the mixture decreased to a level lower than 1.0 mg KOH/g (which took about 6 hours). n-butyl titanate (TBT, 15 ppm in final product) was added into the system when water removal slowed down (ca. 6 h after the reaction started), followed by subjecting the reactor to vacuum (ca. 150 mbar) to accelerate the reduction of acid value. When the acid value of the reaction mixture decreased to be lower than 1.0 mg KOH/g, the reaction was stopped, the final product was cooled down to 80°C, filtered, packaged and sampled for the characterization of acid value, hydroxyl value and viscosity. The polyester polyols prepared in the Comparative Examples 1-2 (Com.Ex.1-2) and Inventive Examples 1-3 (In.Ex.1-3) and are referred as PBA2000, PBMA2000, PEBA2000, PEHA2000 and PEA2000, respectively. All the recipes and characterization results are summarized in Table 2.

Table 2. Recipes and specifications of different polyester polyols.

Example No.	Com. Ex.1	Com. Ex.2	In. Ex.1	In. Ex.2	In. Ex.3
Name of polyester polyol	PBA2000	PBMA2000	PEBA2000	PEHA2000	PEA2000
Adipic acid (AA)	59.48	61.50	63.65	59.50	68.38
Monoethylene glycol (MEG)			14.82	13.96	31.62
2-Methyl-1,3-propane diol (MPO)		17.63			
1,4-Butane diol (BDO)	40.52	20.87	21.53		
1,6-Hexane diol (HDO)				26.54	

Acid Value (mg KOH/g)	0.30	0.90	0.30	0.30	0.20
Hydroxyl Value (mg KOH/g)	56.0	52.0	56.0	56.0	56.0
Viscosity (mPa·s, 75 °C)	730	820	700	750	600

Notes:

a. PBA2000 represents polybutylene adipate with a molecular weight of 2000 g/mol;

b. PBMA2000 represents polybutylene 2-methyl-1,3-propylene adipate with a molecular weight of 2100 g/mol (wherein the BDO/MPO by molar ratio is 1/1);

c. PEBA2000 represents polybutylene ethylene adipate with a molecular weight of 2000 g/mol (wherein the MEG/BDO by molar ratio is 1/1);

d. PEHA2000 represents polyethylene hexylene adipate with a molecular weight of 2000 g/mol (wherein the MEG/HDO by molar ratio is 1/1);

e. PEA2000 represents polyethylene adipate with a molecular weight of 2000 g/mol.

It can be seen that the viscosities of polyester polyols decreased significantly along with the increase in the content of MEG, which is exactly contrary to the theoretical forecast. It is generally believed in the macromolecule technical field that MEG is the shortest dialcohol blocks and thus polyester polyols based on MEG contain the most amount of ester bonds for among the polyester polyol having the same molecular weight. The high ester bond density will cause significant interchain interaction between macromolecular polyester polyols, which is supposed to incur notable increment of viscosity.

2.2 Inventive Examples 4-6 and Comparative Examples 3-4: Synthesis and characterization of prepolymers

Prepolymers were prepared by reaction of various polyols of the above examples with MDI according to the recipes shown in Table 3. Specifically, each of the polyols was preheated to 60 °C for 12 hours before being charged into a tank reactor equipped with a vacuum pump and oil bath. MDI and benzoyl chloride were initially loaded into the reactor and kept at 60 °C with agitation. Polyols were then fed into the reactor and temperature of the system was kept below 75 °C during the feeding process. The mixture was then heated to 80 °C and allowed to react for 150 min with stirring. After that, the system was cooled down to 50 °C, followed by addition of Isonate 143LP and Isonate PR 7020 and agitation for additional 20 min. Final products were collected characterized for quantification of NCO content and degassing under vacuum for 30 min.

Table 3. Recipes and characterization results of the prepolymers.

Example No.	Com.Ex. 3	Com.Ex. 4	In.Ex. 4	In.Ex. 5	In.Ex. 6
	Prepolymer-a (based on PBA2000)	Prepolymer-b (based on of PBMA2000)	Prepolymer-c (based on PEBA2000)	Prepolymer-d (based on PEHA2000)	Prepolymer-e (based on PEA2000)
Isonate M125	56.295	56.295	56.295	56.295	56.295
Benzoyl Chloride	0.005	0.005	0.005	0.005	0.005
Isonate 143LP	4.000	4.000	4.000	4.000	4.000
Isonate PR 7020	2.500	2.500	2.500	2.500	2.500
PBA2000	37.200				
PBMA2000		37.200			
PEBA2000			37.200		
PEHA2000				37.200	
PEA2000					37.200
NCO Content (wt. %)	19.060	19.220	19.000	18.930	18.880
Viscosity (mPa·s, 25 °C)	1225.000	1300.000	1100.000	1225.000	975.000

As shown in Table 3, prepolymers based on higher MEG contents show decreased viscosities.

2.3 Inventive Examples 7-9 and Comparative Examples 5-6: Study on the compatibility between polyester polyols and polyether polyols

A mixture mainly consisting of polyether polyols as shown in Table 4 was formulated and blended with the polyester polyols prepared in the previous inventive examples 1-3 and comparative examples 1-2 to characterize the compatibility therebetween, wherein score 1 represents occurrence of severe phase-separation, score 2 represents occurrence of slight phase-separation, and score 3 represents no occurrence of phase-separation.

As shown in Table 4, the polyester polyols of comparative examples 1-2, which do not comprise repeating units derived from MEG, showed limited compatibility with polyether polyols, whereas the polyester polyols of Inventive Examples 1~3, which comprise 50-100 mol% of repeating units defined from MEG, showed satisfactory compatibility with polyether polyols.

Table 4. Compatibility study of various polyester polyols with polyether polyols.

Example No.	Com.Ex.5	Com.Ex.6	In.Ex.7	In.Ex.8	In.Ex.9
Polyether polyol mixture					
PTMEG2000	22.00	22.00	22.00	22.00	22.00
DNC 701	22.40	22.40	22.40	22.40	22.40
CP 6001	42.19	42.19	42.19	42.19	42.19

BDO	11.90	11.90	11.90	11.90	11.90
Dabco 33s	0.25	0.25	0.25	0.25	0.25
Niax A-1	0.15	0.15	0.15	0.15	0.15
Polycat 77	0.45	0.45	0.45	0.45	0.45
Dabco DC-1	0.04	0.04	0.04	0.04	0.04
Tegostab B-8408	0.10	0.10	0.10	0.10	0.10
Fomrez UL 38	0.03	0.03	0.03	0.03	0.03
Lithene N4-9000	0.80	0.80	0.80	0.80	0.80
Water	0.30	0.30	0.30	0.30	0.30
Polyester polyols					
PBA2000	28.20				
PBMA2000		28.20			
PEBA2000			28.20		
PEHA2000				28.20	
PEA2000					28.20
Mol. content MEG in alcohols for polyesterols	0	0	50%	50%	100%
Mixing temperature (°C)	80	80	80	80	80
Mixing condition	Mixtures were prepared using a DAC 150.1 FVZ Flack Tec speed mixer at 2500 rpm for 1.5 min.				
Storage temperature (°C)	80	80	80	80	80
Storage time (h)	6	6	6	6	6
Compatibility Score[1]	1	1	2	2-3	3

2.4 Inventive Examples 10-12 and Comparative Examples 7-8: Synthesis and Characterization of polyurethane elastomers

Polyol components were made beforehand according to the recipes shown in Table 5 by mixing polyols, chain extenders, catalysts, blowing agents and silicon-based additives together. Polyurethane elastomers were then prepared via mixing of the polyol components with pre-synthesized prepolymers at 50 °C and injection of the mixture into a metal mold at 50 °C using a low pressure machine (Green). Reactions between the polyol components and the prepolymers occurred instantly after the mixing, and the molded samples were demolded after being cured at 50°C for 5 min. The post-cured samples were stored for at least 24 h at room temperature before testing.

Table 5. Formulations and characterization of polyurethane elastomers.

Example No.	Com. Ex.7	Com. Ex.8	In.Ex.10	In.Ex.11	In.Ex.12
Polyol Component					
PTMEG2000	22.00	22.00	22.00	22.00	22.00
DNC 701	22.40	22.40	22.40	22.40	22.40
CP 6001	42.19	42.19	42.19	42.19	42.19
BDO	11.90	11.90	11.90	11.90	11.90
Dabco 33s	0.25	0.25	0.25	0.25	0.25
Niax A-1	0.15	0.15	0.15	0.15	0.15
Polycat 77	0.45	0.45	0.45	0.45	0.45

Dabco DC-1	0.04	0.04	0.04	0.04	0.04
Tegostab B-8408	0.10	0.10	0.10	0.10	0.10
Fomrez UL 38	0.03	0.03	0.03	0.03	0.03
Lithene N4-9000	0.80	0.80	0.80	0.80	0.80
Water	0.30	0.30	0.30	0.30	0.30
Prepolymer Component					
PBA2000 Prepolymer	77.90				
PBMA2000 Prepolymer		77.25			
PEBA2000 Prepolymer			78.14		
PEHA2000 Prepolymer				78.43	
PEA2000 Prepolymer					78.64
Ratio of OH/NCO	1/1	1/1	1/1	1/1	1/1
Hardness (Asker C)	79	79	79	79	79
Tensile strength (kgf/cm^2)	37	45	49	46	40
Elongation (%)	174	330	242	256	284
Tear strength (N/cm)	222	223	222	233	249
Abrasion Loss (mm^3)	316	178	295	184	162
Loss Compliance ($\times 10^{-8}$, Pa^{-1})	8.23	9.29	7.81	5.67	3.30

Table 5 showed the compositions and performances of the resultant polyurethanes made from polyol components and various prepolymers. The Comparative Examples 7 and 8, which were based on polyols other than the polyester polyol of the present disclosure, exhibited inferior tear strength, while the Inventive Examples 10-12, which comprised the unique polyester polyol of the present disclosure, could achieve much higher tear strength. The tear strength increased along with the increase of repeating units derived from MEG in the polyester polyols, and the polyester polyols with pure MEG showed the highest tear strength. The dynamic properties of each sample were also characterized with the loss compliance value, wherein lower loss compliance values represent better dynamic properties. As can be seen from table 5, the Comparative Examples 7 and 8, which were based on polyols other than the polyester polyol of the present disclosure, exhibited inferior dynamic properties, while the Inventive Examples 10-12, which comprised the unique polyester polyol of the present disclosure, could achieve much better dynamic properties. Besides, the polyester polyols with pure MEG showed the best dynamic properties in the resultant polyurethane materials.

2.5 Inventive Examples 13-15 and Comparative Examples 9-10: Synthesis and

Characterization of polyurethane elastomers

Polyol components were made beforehand according to the recipes shown in Table 6 by mixing polyols, chain extenders, catalysts, blowing agents and silicon-based additives together. The prepolymer used in these inventive examples and comparative examples were commercially purchased. Polyurethane elastomers were then prepared via mixing of the polyol components with the prepolymers at 50 °C and injection of the mixture into a metal mold at 50 °C using a low pressure machine (Green). Reactions between the polyol components and the prepolymer occurred instantly after the mixing, and the molded samples were demolded after being cured at 50°C for 5 min. The post-cured samples were stored for at least 24 h at room temperature before testing.

Table 6. Formulations and characterization of polyurethane elastomers.

Example No.	Com. Ex.9	Com. Ex.10	In.Ex.13	In.Ex.14	In.Ex.15
Polyol Component					
DNC 701	22.4	22.4	22.4	22.4	22.4
CP 6001	35.98	35.98	35.98	35.98	35.98
PBA2000	*28.20*				
PBMA2000		28.20			
PEBA2000			*28.20*		
PEHA2000				28.20	
PEA2000					*28.20*
BDO	11.90	11.90	11.90	11.90	11.90
Dabco 33s	0.25	0.25	0.25	0.25	0.25
Niax A-1	0.15	0.15	0.15	0.15	0.15
Polycat 77	0.45	0.45	0.45	0.45	0.45
Dabco DC-1	0.04	0.04	0.04	0.04	0.04
Tegostab B-8408	0.10	0.10	0.10	0.10	0.10
Fomrez UL 38	0.03	0.03	0.03	0.03	0.03
Lithene N4-9000	0.80	0.80	0.80	0.80	0.80
Water	0.30	0.30	0.30	0.30	0.30
Prepolymer Component					
PTMEG2000 Prepolymer	78.92	78.92	78.92	78.92	78.92
Ratio of OH/NCO	1/1	1/1	1/1	1/1	1/1
Hardness (Asker C)	79	79	79	79	79
Tensile strength (kgf/cm^2)	41	45	43	41	40
Elongation (%)	160	320	280	260	285
Tear strength (N/cm)	210	220	235	240	250
Abrasion Loss (mm^3)	330	190	260	190	130

Loss Compliance ($\times 10^{-8}$, Pa^{-1})	10.05	10.11	6.22	4.53	3.10

As can be seen from table 6, the polyurethane elastomers prepared by using the unique polyester polyol/polyether polyol physical blend of the present disclosure can achieve superior tear strength, abrasion resistance and dynamic properties at least no worse than the polyurethane elastomers derived from polyester-polyether polyol copolymer, thus the present disclosure has successfully provided a cost-effective and simple means for improving the performance properties of the polyurethane elastomers.

What is claimed is:

1. A polyol composition comprising:

(A) a first polyester polyol derived from (i) at least one C_2-C_{20} multifunctional carboxylic acid, anhydride thereof, derivative thereof, or a blend thereof, and (ii) at least one aliphatic polyol compound;

(B) at least one first polyether polyol;

wherein the aliphatic polyol compound comprises at least 50wt% of monoethylene glycol, based on the total weight of the aliphatic polyol compound; and

wherein the first polyester polyol and the first polyether polyol are not covalently bonded.

2. The polyol composition according to claim 1, wherein the aliphatic polyol compound comprises at least 50wt% of monoethylene glycol and up to 50wt% of at least one co-polyol compound, based on the total weight of the aliphatic polyol compound, and

wherein the co-polyol compound is selected from a group consisting of a C_3-C_{20} aliphatic multifunctional alcohol, C_3-C_{20} alicyclic multifunctional alcohol, C_7-C_{20} aromatic multifunctional alcohol, dimer thereof, trimer thereof, and a blend thereof.

3. The polyol composition according to claim 1, wherein the aliphatic polyol compound comprises 100wt% of monoethylene glycol, based on the total weight of the aliphatic polyol compound.

4. The polyol composition according to claim 1, wherein the first polyether polyol is derived from a polycondensation reaction of at least one raw material selected from the group consisting of C_2-C_{10} alkylene oxide, C_2-C_{12} alkylene glycol, C_2-C_{10} aliphatic triol, C_2-C_{10} aliphatic tetraol, and a blend thereof.

5. A polyurethane composition, comprising

(I) an isocyanate component comprising at least one prepolymer having at least two free isocyanate groups, wherein the prepolymer is prepared by reacting a first isocyanate

compound having at least two free isocyante groups with at least one first isocyanate-reactive compound; and

(II) an isocyanate-reactive component;

wherein at least one of the first isocyanate-reactive compound and the isocyanate-reactive component comprises a first polyester polyol derived from (i) at least one C_2-C_{20} multifunctional carboxylic acid, anhydride thereof, derivative thereof, or a blend thereof, and (ii) at least one aliphatic polyol compound; and

wherein the aliphatic polyol compound comprises at least 50wt% of monoethylene glycol, based on the total weight of the aliphatic polyol compound.

6. A polyurethane composition, comprising

(I) an isocyanate component comprising at least one prepolymer having at least two free isocyanate groups, wherein the prepolymer is prepared by reacting a first isocyanate compound having at least two free isocyante groups with at least one first isocyanate-reactive compound; and

(II) an isocyanate-reactive component;

wherein at least one of the first isocyanate-reactive compound and the isocyanate-reactive component comprises the polyol composition according to claim 1.

7. The polyurethane composition according to claim 6, wherein at least one of the first isocyanate-reactive compound and the isocyanate-reactive component comprises a second polyol compound selected from the group consisting of a C_2-C_{16} aliphatic polyhydric alcohol comprising at least two hydroxyl groups, a C_6-C_{15} cycloaliphatic or aromatic polyhydric alcohol comprising at least two hydroxyl groups, a C_7-C_{15} araliphatic polyhydric alcohol comprising at least two hydroxyl groups, a polyester polyol which is different from the first polyester polyol and has a molecular weight from 100 to 5,000 and an average hydroxyl functionality of 1.5 to 5.0, a polyether which is different from the first polyether polyol, and combinations thereof.

8. The polyurethane composition according to claim 6, wherein the isocyanate component optionally further comprises at least one second monomeric isocyanate compound

having at least two free isocyante groups, and

wherein the first isocyanate compound and the second monomeric isocyanate compound are separately selected from the group consisting of C_2-C_{12} aliphatic polyisocyanate comprising at least two isocyanate groups, C_6-C_{15} cycloaliphatic or aromatic polyisocyanate comprising at least two isocyanate groups, C_7-C_{15} araliphatic polyisocyanate comprising at least two isocyanate groups, and any combinations thereof.

9. A method for preparing a polyurethane material with the polyurethane composition according to claim 6, comprising a step of combining (I) the isocyanate component with (II) the isocyanate-reactive component.

10. A polyurethane material prepared with the method according to claim 9.

11. A method for enhancing the compatibility between a polyester polyol and a polyether polyol, comprising:

(a) reacting at least one C_2-C_{20} multifunctional carboxylic acid, anhydride thereof, derivative thereof, or a blend thereof with at least one aliphatic polyol compound to form a first polyester polyol, wherein the aliphatic polyol compound comprises at least 50wt% of monoethylene glycol, based on the total weight of the aliphatic polyol compound;

(b) providing at least one first polyether polyol; and

(c) physically blending the first polyester polyol with the first polyether polyol;

wherein the first polyester polyol and the first polyether polyol are not covalently bonded.

INTERNATIONAL SEARCH REPORT

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PCT/CN2020/102012

A. CLASSIFICATION OF SUBJECT MATTER

C08G 18/42(2006.01)i; C08G 18/48(2006.01)i

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 18

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)

CNPAT,CNKI,WPI,EPODOC: adipate, adipic, PEA, PEHA, PEBA, +ethylene d glycol, +isocyanate, polyester, polyether, polyol, prepolymer+

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 109608605 A (TRANSFAR ZHILIAN CO. LTD.) 12 April 2019 (2019-04-12) description, paragraph 0076	1-11
X	CN 104893537 A (JIANGSU NO.2 NORMAL COLLEGE et al.) 09 September 2015 (2015-09-09) description, paragraphs 0025 and 0028	1-11
X	CN 101704936 A (SINOCHEM INTERNAT. SUZHOU NEW MATERIAL R&D CO. LTD.) 12 May 2010 (2010-05-12) description, paragraphs 0024-0044	1-11
X	CN 104004142 A (ZHEJIANG TRANSFAR CO. LTD.) 27 August 2014 (2014-08-27) description, paragraph 0048	1-11
X	CN 103102468 A (ZHEJIANG TECHNOLOGY UNIV.) 15 May 2013 (2013-05-15) description, paragraphs 0036-0070	1-11
X	CN 110713808 A (CHONGQING HANTUO TECHNOLOGY CO. LTD.) 21 January 2020 (2020-01-21) description, paragraphs 0037-0042	1-11

☑ 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
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"P" document published prior to the international filing date but later than the priority date claimed
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"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	Date of mailing of the international search report
15 March 2021	**26 March 2021**
Name and mailing address of the ISA/CN **National Intellectual Property Administration, PRC** **6, Xitucheng Rd., Jimen Bridge, Haidian District, Beijing** **100088** **China**	Authorized officer **HU,Xinliang**
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PCT/CN2020/102012

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A	US 2014343224 A1 (NAT INST. CHUNG SHAN SCIENCE & TECHNOLOGY) 20 November 2014 (2014-11-20) description, paragraphs 0083-0092	1-11
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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2020/102012

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				EP	3109269	A1	28 December 2016