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(54) **Title:** POLYURETHANE COMPOSITIONS, PRODUCTS PREPARED WITH SAME AND PREPARATION METHODS THEREOF

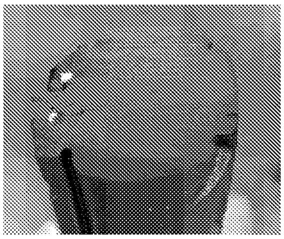

Figure 4

(57) **Abstract:** A polyurethane composition is provided. The polyurethane composition comprises (A) one or more polyurethane-prepolymers prepared by reacting at least one polyisocyanate compound with a first polyol component; and (B) a second polyol component; wherein at least one of the first polyol component and the second polyol component comprises an ester/ether block copolymer polyol synthesized by reacting a starting material polyether polyol with a C_4-C_{20} lactone. The polyurethane foam prepared by using the polyurethane composition can achieve inhibited internal heat buildup, high thermal stability and superior tear strength. A polyurethane product prepared with said foam, a method for preparing the polyurethane foam and a method for improving the performance property of the polyurethane foam are also provided.

POLYURETHANE COMPOSITIONS, PRODUCTS PREPARED WITH SAME AND PREPARATION METHODS THEREOF

FIELD OF THE INVENTION

The present disclosure relates to a polyurethane composition, a polyurethane foam and a molded product prepared by using the composition, a method for preparing the polyurethane foam and a method for improving the performance properties of the polyurethane foam. The polyurethane composition exhibits decreased viscosity, and the polyurethane foam exhibits excellent properties such as inhibited internal heat buildup, high thermal stability, superior tear strength, enhanced abrasion resistance and good hydrolysis resistance.

BACKGROUND TECHNOLOGY

Microcellular polyurethane foams are foamed polyurethane materials with a density of about 100-900 kg/m^3 and 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 polyurethane-prepolymers obtained by reacting polyols with polyisocyanates. The two components are blended at high speed and then transferred into varied molds with desired shapes. Over the past decades, microcellular polyurethane foams have been employed in a wide range of end use applications like shoemaking (e.g., soles) and automotive industries (e.g., bumpers and arm rests of integral skin foams). Recently, microcellular polyurethane foams have been explored in solid tire applications. These microcellular polyurethane solid tires have been attractive due to the possibility of eliminating deflation risk that all the pneumatic rubber tires inherently possess and may bring about potential safety issues and increased maintenance costs.

The uses of polyurethane in tire applications have been challenging due to inherent attributes of polyurethanes to generate “internal heat”. The internal heat buildup originates from transition of mechanical energy into heat inside polyurethanes and is characterized by significant augmentation of the tire temperature during rolling especially under high speed and load. With increasing temperature, material failures including fatigue cracking and/or melting are usually observed. Thus the upper limits of speed and load under which a polyurethane tire can operate are determined by internal heat buildup, and of course, thermal stability of the polyurethane tire. Significant efforts have been made to increase the thermal stability of polyurethanes by introduction of functional moieties e.g. isocyanurate, oxazolidone, oxamide or borate groups or to reduce the "internal heat buildup" in polyurethanes by using special isocyanates like 1,5-naphthylene diisocyanate. However, the above indicated modification by using the chemicals with special groups or special isocyanates are usually too expensive to be commercialized.

Notably, it was reported that formulations based on mixtures of polyester and polyether polyols were good candidates for manufacturing the polyurethane solid tires. These tires showed good modality, abrasion-resistance, puncture-resistance, high resilience, and low compression set. However, blends of polyether polyols and polyester polyols tend to bring about disadvantages in processing properties like short operation time due to segmentation and deteriorated performance balance between tear strength, internal heat buildup and thermal-stability, which might be attributed to the incompatibility nature between polyether and polyester structures.

For the above reasons, there is still a need in the polyurethane manufacture industry to develop 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 polyurethane composition which can achieve one or more of the above targets.

SUMMARY OF THE INVENTION

The present disclosure provides a unique polyurethane composition, a polyurethane foam and a molded product prepared by using the composition, a method for preparing the polyurethane foam and a method for improving the performance properties of the polyurethane foam.

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

(A) one or more polyurethane-prepolymers prepared by reacting at least one polyisocyanate compound with a first polyol component; and

(B) a second polyol component;

wherein at least one of the first polyol component and the second polyol component comprises an ester/ether block copolymer polyol synthesized by reacting a starting material polyether polyol with a C_4-C_{20} lactone optionally substituted with one or more substituents selected from the group consisting of C_1-C_{12} alkyl, C_2-C_{12} alkenyl, nitrogen-containing group, phosphorous-containing group, sulfur-containing group and halogen. According to a preferable embodiment of the present disclosure, the starting material polyether polyol is a poly(C_2-C_{10})alkylene glycol, a copolymer of multiple (C_2-C_{10})alkylene glycols or a polymer polyol having a core phase and a shell phase based on the poly(C_2-C_{10})alkylene glycol or copolymer thereof, examples of the poly(C_2-C_{10})alkylene glycol or copolymer thereof may include polyethylene glycol, polypropylene glycol, polytetramethylene glycol, poly(2-methyl-1,3-propane glycol), and poly(ethylene oxide-polypropylene oxide) glycol, wherein the starting material polyether polyol has a molecular weight of 100 to 5,000, preferably 200 to 3,000 and an average hydroxyl functionality of 1.5 to 5.0; the C_4-C_{20} lactone is selected from the group consisting of β-butyrolactone, γ-butyrolactone, γ-valerolactone, Ɛ-caprolactone, γ-caprolactone, γ-octalactone, γ-decalactone, γ-dodecalactone, and any combinations thereof, all the above stated lactones can be optionally substituted, such as being substituted with the group consisting of C_1-C_{12} alkyl, C_2-C_{12} alkenyl, nitrogen-containing group, phosphorous-containing group, sulfur-containing group and halogen. According to another preferable embodiment of the present disclosure, the ester/ether block copolymer polyol has a molecular weight of at least 800 g/mol and an average hydroxyl functionality of 1.5 to 5.0, and the weight ratio between the starting material polyether polyol and the C_4-C_{20} lactone is from 0.05/0.95 to 0.95/0.05.

In a second aspect of the present disclosure, the present disclosure provides a microcellular polyurethane foam prepared with the polyurethane composition as stated above, wherein repeating units derived from the ester/ether block copolymer polyol are included in the polyurethane main chain of the polyurethane microcellular polyurethane foam.

In a third aspect of the present disclosure, the present disclosure provides a molded product prepared with the above indicated microcellular polyurethane foam, wherein the molded product is selected from the group consisting of tire, footwear, sole, furniture, pillow, cushion, toy and lining.

In a fourth aspect of the present disclosure, the present disclosure provides a method for preparing the microcellular polyurethane foam, comprising the steps of:

i) reacting at least one polyisocyanate compound with a first polyol component to form the polyurethane-prepolymer; and

ii) reacting polyurethane-prepolymer with a second polyol component to form the microcellular polyurethane foam;

wherein repeating units derived from the ester/ether block copolymer polyol are covalently linked in the polyurethane main chain of the polyurethane microcellular polyurethane foam.

In a fifth aspect of the present disclosure, the present disclosure provides a method for improving the performance property of a microcellular polyurethane foam, comprising the step of including repeating units derived from a ester/ether block copolymer polyol synthesized by reacting a starting material polyether polyol with a C_4-C_{20} lactone in the polyurethane main chain of the polyurethane microcellular polyurethane foam, wherein the performance property includes at least one of internal heat buildup, thermal stability, tear strength, viscosity, abrasion resistance and hydrolysis resistance.

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.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows the reaction scheme for the preparation of the ester/ether block copolymer polyol;

Fig. 2-3 show the photographs of polyurethane solid tires prepared by using materials with no ester/ether block copolymer polyol;

Fig. 4-7 show the photographs of polyurethane solid tires prepared by embodiments according to the present disclosure.

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. In the context of the present disclosure, the ester/ether block copolymer polyol derived from the reaction between a starting material polyether polyol and an optionally substituted C_4-C_{20} lactone is referred as “the ester/ether block copolymer polyol” for short.

According to an embodiment of the present disclosure, the polyurethane composition is a "two-component", "two-part" or "two-package" composition comprising at least one polyurethane-prepolymer component (A) and an isocyanate-reactive component (B), wherein the polyurethane-prepolymer comprises free isocyanate groups and is prepared by reacting at least one polyisocyanate compound with a first polyol component, and the isocyanate-reactive component (B) is a second polyol component. The polyurethane-prepolymer 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 an ester/ether block copolymer polyol derived from the reaction between a starting material polyether polyol and an optionally substituted C_4-C_{20} lactone is included in at least one of the first polyol component and the second polyol component to incorporate repeating units (residual moiety) of said ester/ether block copolymer polyol in the polyurethane main chain of the final polyurethane foam, thus the performance properties of the polyurethane foam can be effectively improved. According to one embodiment of the present disclosure, the first polyol component comprises the ester/ether block copolymer polyol derived from the reaction between a starting material polyether polyol and an optionally substituted C_4-C_{20} lactone, while the second polyol component does not. According to an alternative embodiment of the present disclosure, the second polyol component comprises the ester/ether block copolymer polyol derived from the reaction between a starting material polyether polyol and an optionally substituted C_4-C_{20} lactone, while the first polyol component does not. According to an alternative embodiment of the present disclosure, both the first and the second polyol component comprise the ester/ether block copolymer polyol derived from the reaction between a starting material polyether polyol and an optionally substituted C_4-C_{20} lactone. The ring-opening polymerization reaction scheme for preparing the ester/ether block copolymer polyol is illustrated in Fig. 1, wherein the polyether polyols and lactones are combined and heated in the presence of a catalyst to produce the ester/ether block copolymer polyol having more than one free hydroxyl terminate group as well as the residual moieties of the polyether polyol and the lactone. It is to be particularly emphasized that the inclusion of such an ester/ether block copolymer polyol moiety in the polyurethane main chain has not been disclosed in the prior art. For example, due to the high reactivity between the isocyanate group and the isocyanate-reactive group, the reaction between the polyisocyanate compound and e.g. a polyether polyol/lactone physical blend, a polyether polyol/polyester polyol physical blend or a polyether polyol/polyhydric alcohol/polyhydric carboxylic acid physical blend can never form the above indicated residual moiety of the ester/ether block copolymer polyol.

In various embodiments, the starting material polyether polyol used for preparing the ester/ether block copolymer polyol has a molecular weight of 100 to 5,000 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 and 5000 g/mol. In various embodiments, the starting material polyether polyol used for preparing the ester/ether block copolymer 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 starting material polyether polyol is 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 another embodiment of the present application, starting material polyether polyol can be a polymer polyol having a core phase and a shell phase based on the poly(C_2-C_{10})alkylene glycol or copolymer thereof.

preferably, the polymer polyol has a core phase and a shell phase based on the poly(C_2-C_{10})alkylene glycol or copolymer thereof, having a solid content of 1-50%, an OH value 10 ~ 149, and a hydroxyl functionality of 1.5-5.0. In the context of the present disclosure, the above stated polymer polyol for the starting material polyether polyol refers to a composite particulate having a core-shell structure. The shell phase may comprise at least one poly(C_2-C_{10})alkylene glycol or copolymer thereof, for example, the polyol may be selected from the group consisting of 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. The core phase may be micro-sized and may comprise any polymers compatible with the shell phase. For example, the core phase may comprise polystyrene, polyacrylnitrile, polyester, polyolefin or polyether different (in either composition or polymerization degree) from those of the shell phase. According to a preferable embodiment of the present application, the polymer polyol is a composite particulate having a core-shell structure, wherein the core is a micro-sized core composed of SAN (styrene and acryl nitrile) and the shell phase is composed of PO-EO polyol. Such a polymer polyol can be prepared by radical copolymerization of styrene, acryl nitrile and poly(EO-PO) polyol comprising ethylenically unsaturated groups.

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 1 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.

In various embodiments, the C_4-C_{20} lactone can be selected from the group consisting of β-butyrolactone, γ-butyrolactone, γ-valerolactone, ε-caprolactone, γ-caprolactone, γ-octalactone, γ-decalactone, γ-dodecalactone, and any combinations thereof, all of these lactones can be optionally substituted with one or more substituents selected from the group consisting of C_1-C_{12} alkyl, C_2-C_{12} alkenyl, nitrogen-containing group, phosphorous-containing group, sulfur-containing group and halogen. In various embodiments of the present disclosure, the nitrogen-containing group includes amino group, imino group, amine group, amide group, imide group or nitro group; the phosphorous-containing group includes phosphine group, phosphoric acid/phosphate group, or phosphonic acid/phosphonate group; the sulfur-containing group includes thiol, sulfonic acid/sulfonate group, or sulfonyl group; and the halogen includes fluorine, chlorine, bromine or iodine.

According to a preferable embodiment, the polyether polyol is the only reactant reacting with the lactone, and no other reactants, such as monomeric alkylene oxide are included in the system for preparing the ester/ether block copolymer polyol. Particularly speaking, the reaction between the polyether polyol and the lactone will form a "block copolymer", while the reaction between the monomeric alkylene oxide and the lactone will form a "random copolymer".

A catalyst can be used in the production of the ester/ether block copolymer polyol. Examples of the catalyst include 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 ester/ether block copolymer polyol prepared by the reaction between the starting material polyether polyol and the lactone can have a molecular weight of larger than 800 g/mol. According to an embodiment of the present disclosure, the weight ratio between the starting material polyether polyol and the C_4-C_{20} lactone is from 0.05/0.95 to 0.95/0.05, preferably from 0.25/0.75 to 0.75/0.25. The weight ratio can be properly adjusted according to the particular functionality and molecular weight of these reactants, with the proviso that the resultant ester/ether block copolymer polyol comprises more than one free hydroxyl groups and has an average hydroxyl functionality of 1.5 to 5.0, such as in the numerical range obtained by combining any two of the following end point values: 1.5, 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.

In various embodiments, the polyisocyanate compound refers to an aliphatic, cycloaliphatic, aromatic or heteroaryl compound having at least two isocyanate groups. In a preferable embodiment, the polyisocyanate 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 polyisocyanate 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 polyisocyanate 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 polyisocyanate 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 first polyol component, the second polyol component, and any additional additives or modifiers.

Additionally or alternatively, the first polyol component and the second polyol component may comprise a polyol other than the ester/ether block copolymer polyol (hereinafter referred as “polyol” for short). According to an embodiment of the present application, the first polyol component exclusively comprises the ester/ether block copolymer polyol while the second polyol component comprises the polyol. According to another embodiment of the present application, the second polyol component exclusively comprises the ester/ether block copolymer polyol while the first polyol component comprises the polyol. According to another embodiment of the present application, both the first and the second polyol component exclusively comprise the ester/ether block copolymer polyol and do not comprise any other polyol as the reactants. According to another embodiment of the present application, the first polyol component comprises the ester/ether block copolymer polyol and the polyol, while the second polyol component comprises the polyol. According to another embodiment of the present application, the second polyol component comprises the ester/ether block copolymer polyol and the polyol, while the first polyol component comprises the polyol. According to another embodiment of the present application, the second polyol component comprises the ester/ether block copolymer polyol and the polyol, and the first polyol component comprises the ester/ether block copolymer polyol and the polyol.

According to various embodiments of the present application, the polyol other than the ester/ether block copolymer polyol 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, polyester polyols having a molecular weight from 100 to 5,000 and an average hydroxyl functionality of 1.5 to 5.0, a polymer polyol having a core phase and a shell phase based on polyol, having a solid content of 1-50%, an OH value 10-149, and a hydroxyl functionality of 1.5-5.0, a supplemental polyether polyol which is a poly(C_2-C_{10})alkylene glycol or a copolymer of multiple (C_2-C_{10})alkylene glycols, and combinations thereof; wherein the supplemental polyether polyol can be identical with or different from the first polyether polyol. In the context of the present disclosure, the above stated polymer polyol for the polyol other than the ester/ether block copolymer polyol refers to a composite particulate having a core-shell structure. The shell phase may comprise at least one polyol other than the ester/ether random copolymer polyol, for example, the polyol may be selected from the group consisting of 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. The core phase may be micro-sized and may comprise any polymers compatible with the shell phase. For example, the core phase may comprise polystyrene, polyacrylnitrile, polyester, polyolefin or polyether different (in either composition or polymerization degree) from those of the shell phase. According to a preferable embodiment of the present application, the polymer polyol is a composite particulate having a core-shell structure, wherein the core is a micro-sized core composed of SAN (styrene and acryl nitrile) and the shell phase is composed of PO-EO polyol. Such a polymer polyol can be prepared by radical copolymerization of styrene, acryl nitrile and poly(EO-PO) polyol comprising ethylenically unsaturated groups.

The polyurethane-prepolymer prepared by reacting the polyisocyanate compound with the first polyol component has a NCO group content of from 2 to 50 wt%, preferably from 6 to 49 wt%.

The reaction between the polyisocyanate compound and the first polyol component, and the reaction between the polyurethane-prepolymer and the second polyol 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 foam. 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 foam. 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 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 and various hydrocarbons, hydrofluorocarbons and hydrochlorofluorocarbons. 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.

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 foam 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.

According another preferable embodiment of the present disclosure, the polyurethane composition does not comprise modifying groups such as isocyanurate, oxazolidone, oxamide or borate groups covalently linked to the polyurethane main chain. According another preferable embodiment of the present disclosure, the polyurethane composition does not comprise special and expensive isocyanates such as 1,5-naphthylene diisocyanate. According to various aspects of the present application, improvement in the performance properties has been successfully achieved without the need of incorporating any special and expensive modifying functional groups in the polyurethane main chain.

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
Pure MDI	ISONATE 125MH	Dow Chemical
Lactone	Ɛ-Caprolactone	Sinopharm Chemical Reagent Co., Ltd
Di-acid	Adipic acid (AA)	Shenma Inc.
Di-alcohol	Methylene glycol (MEG)	Shanghai Tony Trade Co., Ltd.
Esterification catalyst	n-Butyl titanate (TBT)	Merck Inc.
Carbodiimide-modified MDI	Isonate 143LP	Dow Chemical
Carbodiimide-modified MDI	Isonate PR 7020	Dow Chemical
Inhibitor	Benzoyl Chloride	Daejung, Korea
Polyether polyol	Voranol CP 6001	Dow Chemical
Polyether polyol	Voranol 1000LM	Dow Chemical
Polyether polyol	Voranol WD2104	Dow Chemical
Polymer polyol	DNC 701	Dow Chemical
Chain extender	1,4-butane diol (BDO)	BASF
Chain extender	Diethanolamine (DEOA)	Shanghai Tony Trade

		Co., Ltd.
Polyether polyol	Polytetramethylene ether glycol (PTMEG) 2000	Dairen Chemical Corporate, Taiwan
Polyester polyol polyethylene butylene adipate	PEBA 2000, Mn=2,000	Dow Chemical
Polybutadiene liquid polymer	Lithene 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

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. 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 ^{o}C to 600 ^{o}C in air atmosphere. Differential scanning calorimeter (DSC) was performed on a TA Q1500 analyzer with a cooling speed of 10 ^{o}C/min and heating speed of 20 ^{o}C/min under N_2 atmosphere.

Preparation Examples 1-2: Synthesis of ester/ether block copolymer polyols

Two Ester/ether block copolymer polyols according to the present disclosure were synthesized via ring-opening reaction of ε-caprolactone using polyether polyols as macro-initiators according to the following general procedure by using the recipes listed in Table 2: polyether polyol (Voranol 1000LM or Voranol WD2104, 50 wt%), lactone (ε-Caprolactone, 50 wt%) and Esterification catalyst (n-Butyl titanate TBT, 25 ppm based on the total weight of the ester/ether block copolymer polyols) were fed into a steal reactor equipped with a vacuum pump and oil bath under nitrogen atmosphere at room temperature. The system was kept at 120°C with stirring for 17 h, followed by application of vacuum under 150 mbar and further heated at 135 °C for 3 h. The product was cooled down to 80°C, filtered, packaged and sampled for determinations of acid value, hydroxyl value and viscosity. The products prepared in these two Preparation Examples 1-2 are referred as PCPC2000-1 and PCPC2000-2, respectively. All the characterization results were also summarized in Table 2.

Table 2 Recipes and Characterization of the Synthesis of Ester/Ether Block Copolymer Polyols

	Control 1	Control 2	PREP. Ex. 1	PREP. Ex. 2
	PEBA2000	PTMEG2000	PCPC2000-1	PCPC2000-2
Adipic acid (AA)	62.39			
Methylene glycol (MEG)	15.33			
1,4-Butane diol (BDO)	22.28			
ε-Caprolactone			50.00	50.00
Voranol 1000LM			50.00	
Voranol WD2104				50.00
Acid Value (mg KOH/g)	0.82	0.05	0.09	0.05
Hydroxyl Value (mg KOH/g)	55.90	56.00	53.79	54.51
Viscosity (mPa·s, 50 °C)	1668.00	900.00	435.00	645.00

Polyester polyol polyethylene butylene adipate (Mn = 2000, PEBA2000) and PTMEG2000 were used as controls in this invention, and the characterization results of these two controls are also listed in Table 2. It can be unexpectedly seen that PCPC2000-1 and PCPC2000-2 exhibit significantly lower viscosity as compared both of the controls.

Preparation Examples 3-6: Synthesis of Polyurethane-Prepolymer

Four different prepolymers were prepared by reacting the polyols prepared in the above examples as well as PTMEG2000 with MDI according to the following general procedure with the recipes shown in Table 3. MDI (ISONATE 125MH) and inhibitor (benzoyl chloride) were initially loaded into a tank reactor equipped with a vacuum pump and oil bath, and then were kept at a temperature of 60 °C with agitation. The polyol was preheated at 60 °C for 12 hours before being charge into the reactor. The reactor was kept at a temperature below 75 °C during the feeding of said polyols. The mixture was then heated to 80 °C and allowed to react for 150 min with stirring. Then the system was cooled down to 50 °C, into which Isonate 143LP and Isonate PR 7020 were added and the content in the reactor was agitation for another 20 min. Final prepolymer products were obtained subsequently after quantification of NCO content and degassing under vacuum for 30 min. The resultant prepolymer has a NCO content of ca. 19 wt%. The characterization results were summarized in Table 3. Two carbodiimide-modified MDI Isonate 143LP and Isonate PR7020 were incorporated in the prepolymers to improve their storage stability at low temperature.

Table 3. Recipes and Characterization of the Prepolymers.

	Prepolymer-1 (Based on PEBA2000)	Prepolymer-2 (Based on PTMEG2000)	Prepolymer-3 (Based on PCPC2000-1)	Prepolymer-4 (Based on PCPC2000-2)
Isonate 125MH	56.295	56.295	56.295	56.295
Benzoyl Chloride	0.005	0.005	0.005	0.005
Isonate 143LP	4.000	4.000	4.000	4.000
Isonate PR 7020	2.500	2.500	2.500	2.500
PEBA2000	37.200			
PTMEG2000		37.200		
PCPC2000-1			37.200	
PCPC2000-2				37.200
NCO Content (wt. %)	19.000	19.060	18.500	19.000
Viscosity (mPa·s, 25 °C)	1266.000	901.000	375.000	410.000

As shown in Table 3, the Prepolymer-3 and Prepolymer-4, which were based on the copolymer polyols of the present disclosure, showed the lowest viscosities 25 °C compared with Prepolymer-1 and Prepolymer-2, which were based on polyester polyol and PTMEG2000.

Examples 1-6: Preparation of Microcellular Polyurethane Foam

Polyol components were made beforehand according to the recipes shown in Table 4 by mixing polyols, chain extenders, catalysts, surfactants, blowing agents and other additives together. The polyurethane-prepolymers synthesized in the above preparation examples were mixed with the polyol components at 50 °C and the mixture was injected 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 polyurethane foam samples were stored for at least 24 h at room temperature before testing.

As can be seen from the recipes shown in Table 4, Example 1 and Example 2 are comparative examples comprising no ester/ether copolymer polyols according to the present disclosure. In particular, the polyol component of Example 1 and Example 2 was a blend of various polyether polyol, and the polyurethane-prepolymer component of Example 1 and Example 2 was Prepolymer-1 and Prepolymer-2, which were prepared by using polyester polyol PEBA2000 and polyether polyol PTMEG2000, respectively.

Three strategies were adopted in the Inventive Examples 3 to 6. Examples 3 and 4 illustrated specific embodiments of the present disclosure in which the polyurethane-prepolymers (Prepolymer-3 and Prepolymer-4) were prepared by using ester/ether blocky polyols, pure MDI, modified MDI, side reaction inhibitor, and the polyol component comprised polyether polyols, chain extenders, blowing agents, catalysts, foam stabilizers and other additives; namely, Examples 3 and 4 only comprised the ester/ether blocky polyols in the polyurethane-prepolymer component. Example 5 illustrated another specific embodiment of the present disclosure in which the polyurethane-prepolymer (Prepolymer-1) was prepared by using polyester polyols, pure MDI, modified MDI, side reaction inhibitor, and the polyol component comprised ester/ether blocky polyols, chain extenders, blowing agents, catalysts, foam stabilizers and other additives; namely, Example 5 only comprised the ester/ether blocky polyols in the polyol component. Example 6 illustrated another specific embodiment of the present disclosure in which the polyurethane-prepolymer (Prepolymer-3) was prepared by using ester/ether blocky polyols, pure MDI, modified MDI, side reaction inhibitor, and the polyol component comprised ester/ether blocky polyols, chain extenders, blowing agents, catalysts, foam stabilizers and other additives; namely, Example 6 comprised the ester/ether blocky polyols in both the polyurethane-prepolymer component and the polyol component.

The polyurethane foams prepared in Examples 1 to 6 were formed into sample plates having a density of ca. 600 kg/m^3, and the characterization results were summarized in the following Table 4.

Table 4. Formulations and Characterization of Examples 1 to 6

	Chemicals	Example 1 (Comparative)	Example 2 (Comparative)	Example 3 (Inventive)	Example 4 (Inventive)	Example 5 (Inventive)	Example 6 (Inventive)
Polyols	PTMEG2000	22.00	22.00	22.00	22.00		
	DNC 701	22.40	22.40	22.40	22.40		
	CP 6001	42.19	42.19	42.19	42.19		
	PCPC-1					86.57	86.57
Chain Extender	BDO	11.90	11.90	11.90	11.90	10.50	10.50
	DEOA					1.00	1.00
Catalyst & surfactant &blowing agent & additive	Dabco 33s	0.25	0.25	0.25	0.25	0.50	0.50
	Niax A-1	0.15	0.15	0.15	0.15		
	Polycat 77	0.45	0.45	0.45	0.45		
	Dabco DC-1	0.04	0.04	0.04	0.04	0.03	0.03
	Tegostab B-8408	0.10	0.10	0.10	0.10		
	Dabco DC 193					0.30	0.30
	Fomrez UL 38	0.03	0.03	0.03	0.03	0.03	0.03
	Lithene N4-9000	0.80	0.80	0.80	0.80	0.80	0.80
	Water	0.30	0.30	0.30	0.30	0.30	0.30
Polyol Component	Viscosity (mPa·s, 50 °C)	376.50	376.50	376.50	376.50	245.50	245.50
Prepolymer	Prepolymer-1	76.61				87.40	
	Prepolymer-2		76.37				
	Prepolymer-3			78.67			90.16
	Prepolymer-4				78.05		
Condition	Mol_{NCO}/Mol_{OH}	1.00	1.00	1.00	1.00	1.00	1.00
	Temperature (°C)	50.00	50.00	50.00	50.00	50.00	50.00
Property	Molded Density (kg/m^3)	600.00	600.00	600.00	600.00	600.00	600.00
	Ester content (%)	16.08	0	8.0	12.8	40.70	32.41
	Hardness (Asker C)	79	81	80	79	72	73
	Tensile Strength (kgf/cm^2)	42	49	47	50	43	43
	Elongation (%)	220	254	283	352	532	401
	Tear Strength (N/cm)	205	270	243	244	243	232
	Thermal Stability[a]	moderate	bad	moderate	excellent	excellent	excellent
	Internal heat buildup[b]	high	low	low	moderate	moderate	moderate

Notes: a. The thermal stability was measured by using the TGA and DSC; and
b. The internal heat buildup was characterized by DMA.

With regard to the tear strength, it can be seen from Table 4 that the samples prepared in Examples 3-6, which comprised the ester/ether block copolymer polyols according to the present disclosure in the polyurethane main chain, exhibited significantly higher values of tear strength than that of Comparative Example 1, which solely adopted traditional polyether and polyester polyols. Besides, Examples 3-6 exhibited higher thermal stabilities as characterized with TGA and DSC than those of Examples 1-2, indicating that the improvement in thermal stability could be attributed to dispersion of more contents of hard domains into the soft phases. The hard domains acted as "enhancing points" so that tear strength was greatly improved.

Examples 1 and 2 exhibited similar phase separation property as indicated by similar thermal property, which could be attributed the incompatibility between polyester and polyether polyols in Example 1. Example 2, which was prepared by using polyether polyols, showed the worst thermal stability at high temperatures. In other words, the samples prepared in the Inventive Examples 3-6 can achieve improved thermal stability over that of the Comparative Example 2.

Generally, the Inventive Examples 3-6, which comprised the ester/ether block copolymer polyols according to the present disclosure in the polyurethane main chain, showed significantly lower internal heat build-up compared to Example 1. Furthermore, the comparison between Example 3 and Example 4 showed that Example 3 exhibited lower internal heat build-up which could be attributed to better phase separation in Example 3 as indicated by significantly higher thermal stability.

Preparation and Characterization of Polyurethane Tires.

Polyurethane solid tires with a diameter of 24 inches and a molded density of 350 kg/m^3 were fabricated in a customer site by using the samples obtained in the above Examples 1 to 6 and characterized by rolling test to evaluate the comprehensive performances thereof. The rolling test was conducted with a line speed of 30 km/h, 65 kg load and two 10-mm high obstacles and lasted for 1 h at room temperature. The testing conditions and characterization results were summarized in Table 5.

Table 5. Rolling test results of the soil tires prepared with the materials of Examples 1-6.

Items	Example 1 (Comparative)	Example 2 (Comparative)	Example 3 (Inventive)	Example 4 (Inventive)	Example 5 (Inventive)	Example 6 (Inventive)
Line Speed (km/h)	30	30	30	30	30	30
Load (kg)	65	65	65	65	65	65
Obstacles (sets)	2	2	2	2	2	2
Obstacle Height (mm)	10	10	10	10	10	10
Rolling Time (h)	1	1	1	1	1	1
Impacts Times	25,150	25,150	25,150	25,150	25,150	25,150
Results	Failed (Molten)	Failed (Molten)	Passed	Passed	Passed	Passed
	Figure 2	Figure 3	Figure 4	Figure 5	Figure 6	Figure 7

The tire samples prepared by using the polyurethane foams of Example 1 and Example 2 showed molten cores after the rolling tests. Core-melting of Example 1 could be attributed to the high internal heat buildup inclination as indicated by the high value of hysteresis. Core-melting of Example 2 could be attributed to the poor thermal stability at high temperatures as indicated by the TGA results. The tire samples prepared by using the polyurethane foams of Inventive Examples 3-6 passed the rolling tests due to good performance balance among tear strength, internal heat buildup and thermal stability at high temperatures.

Conclusions

In view of the above, the ester/ether random copolymer polyols imparted excellent processing and storage stability of the urethane system and outstanding performance balance among high tear strength, high abrasion resistance, low internal heat buildup and high thermal-stability of the final polyurethane material, favoring production of microcellular parts and useful in lots of relevant applications like solid tires.

What is claimed is:

1. A polyurethane composition, comprising

(A) one or more polyurethane-prepolymers prepared by reacting at least one polyisocyanate compound with a first polyol component; and

(B) a second polyol component;

wherein at least one of the first polyol component and the second polyol component comprises an ester/ether block copolymer polyol synthesized by reacting a starting material polyether polyol with a C_4-C_{20} lactone optionally substituted with one or more substituents selected from the group consisting of C_1-C_{12} alkyl, C_2-C_{12} alkenyl, nitrogen-containing group, phosphorous-containing group, sulfur-containing group and halogen.

2. The polyurethane composition according to claim 1, wherein the polyisocyanate compound is selected from the group consisting of C_4-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.

3. The polyurethane composition according to claim 1, wherein the starting material polyether polyol is a poly(C_2-C_{10})alkylene glycol, a copolymer of multiple (C_2-C_{10})alkylene glycols or a polymer polyol having a core phase and a shell phase consisting of the poly(C_2-C_{10})alkylene glycol or copolymer thereof, wherein the starting material polyether polyol has a molecular weight of 100 to 5,000 and an average hydroxyl functionality of 1.5 to 5.0.

4. The polyurethane composition according to claim 1, wherein the starting material polyether polyol is selected from the group consisting of polyethylene glycol, polypropylene glycol, polytetramethylene glycol, poly(2-methyl-1,3-propane glycol), and any copolymers thereof, and wherein the starting material polyether polyol has a molecular weight of 200 to 3,000 and an average hydroxyl functionality of 1.5 to 5.0.

5. The polyurethane composition according to claim 1, wherein the C_4-C_{20} lactone is

selected from the group consisting of β-butyrolactone, γ-butyrolactone, γ-valerolactone, ε-caprolactone, γ-caprolactone, γ-octalactone, γ-decalactone, γ-dodecalactone, and any combinations thereof, optionally substituted with one or more substituents selected from the group consisting of C_1-C_{12} alkyl, C_2-C_{12} alkenyl, nitrogen-containing group, phosphorous-containing group, sulfur-containing group and halogen.

6. The polyurethane composition according to claim 1, wherein the ester/ether block copolymer polyol has a molecular weight of at least 800 g/mol and an average hydroxyl functionality of 1.5 to 5.0, and the weight ratio between the starting material polyether polyol and the C_4-C_{20} lactone is from 0.05/0.95 to 0.95/0.05.

7. The polyurethane composition according to claim 1, wherein at least one of the first polyol component and the second polyol component comprises a polyol other than the ester/ether block copolymer polyol, selecting 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, polyester polyols having a molecular weight from 100 to 5,000 and an average hydroxyl functionality of 1.5 to 5.0, a polymer polyol having a core phase and a shell phase based on polyol, a supplemental second polyether polyol which is a poly(C_2-C_{10})alkylene glycol or a copolymer of multiple (C_2-C_{10})alkylene glycols, and combinations thereof; wherein the supplemental polyether polyol is identical with or different from the starting material polyether polyol.

8. A microcellular polyurethane foam prepared with the polyurethane composition according to any of claims 1 to 7, wherein repeating units derived from the ester/ether block copolymer polyol are covalently linked in polyurethane main chain of the polyurethane microcellular polyurethane foam, and the microcellular polyurethane foam has a density of 100-900 kg/m^3.

9. A molded product prepared with the microcellular polyurethane foam according to claim 8, wherein the molded product is selected from the group consisting of tire, footwear,

sole, furniture, pillow, cushion, toy and lining.

10. A method for preparing the microcellular polyurethane foam according to claim 8, comprising the steps of:

i) reacting at least one polyisocyanate compound with a first polyol component to form the polyurethane-prepolymer; and

ii) reacting the polyurethane-prepolymer with the second polyol component to form the microcellular polyurethane foam;

wherein repeating units derived from the ester/ether block copolymer polyol are covalently linked in polyurethane main chain of the polyurethane microcellular polyurethane foam.

11. A method for improving the performance property of a microcellular polyurethane foam, comprising the step of covalently linking repeating units derived from a ester/ether block copolymer polyol synthesized by reacting a starting material polyether polyol with a C_4-C_{20} lactone in the polyurethane main chain of the polyurethane microcellular polyurethane foam, wherein the performance property includes at least one of internal heat buildup, thermal stability, tear strength, viscosity, abrasion resistance and hydrolysis resistance.

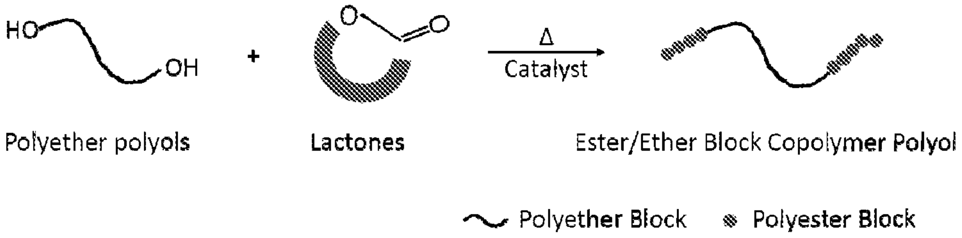

Figure 1

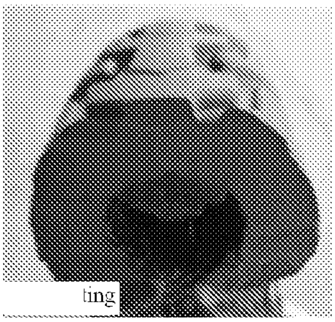

Figure 2

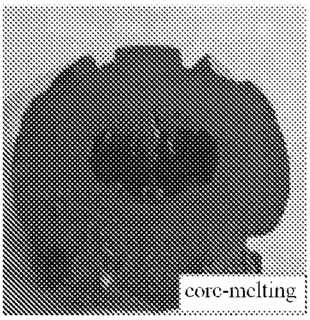

Figure 3

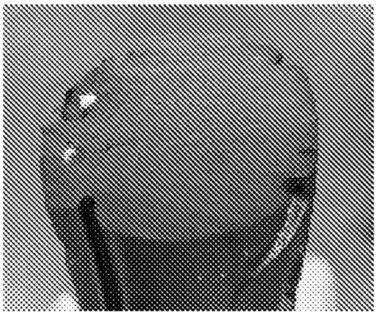

Figure 4

Figure 5

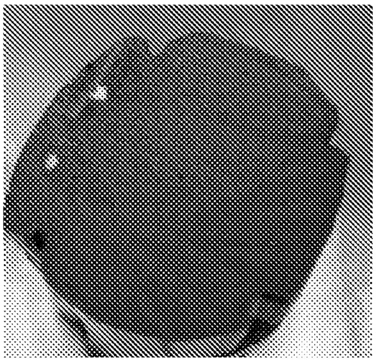

Figure 6

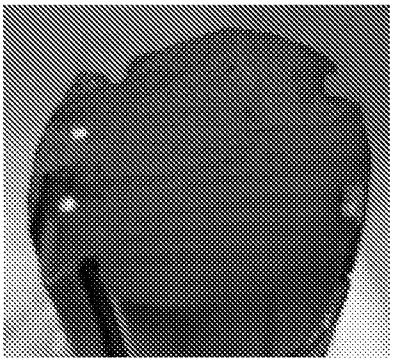

Figure 7

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2019/097014

A. CLASSIFICATION OF SUBJECT MATTER

C08G 18/48(2006.01)i; C08L 75/04(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 C08L

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)

DWPI;SIPOABS;STN;ISI Web of Knowledge;CNABS;CNKI,ester, polyol, addition, polyether, polyurethane, lactone, prepolymer, cellular, polyether polyol, foam, porous, PU, caprolactone, isocyanate

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 107602817 A (ZHUZHOU TIMES NEW MATERIAL TECHNOLOGY CO) 19 January 2018 (2018-01-19) paragraphs 0006-0029	1-11
X	CN 102741311 A (DAINIPPON INK & CHEMICALS) 17 October 2012 (2012-10-17) example 1, paragraphs 0030-0065	1-11
X	JP 1045864 A (DAINIPPON INK & CHEMICALS) 17 February 1998 (1998-02-17) examples 2, 3, 5	1-11
X	JP 04164914 A (DAINIPPON INK & CHEMICALS) 10 June 1992 (1992-06-10) examples 1-6	1-11
A	CN 104672418 A (SHANGHAI HUAFENG MATERIAL SCIENCE TECHNOLOGY RES INST) 03 June 2015 (2015-06-03) the whole document	1-11
A	CN 107141435 A (SHANDONG INOV NEW MATERIALS CO LTD) 08 September 2017 (2017-09-08) the whole document	1-11
A	US 2013053463 A1 (GRAMELLINI ALESSANDRO et al.) 28 February 2013 (2013-02-28) the whole document	1-11

☑ Further documents are listed in the continuation of Box C. ☑ See patent family annex.

*	Special categories of cited documents:	"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
"A"	document defining the general state of the art which is not considered to be of particular relevance	"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
"E"	earlier application or patent but published on or after the international filing date	"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
"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)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search **10 April 2020**	Date of mailing of the international search report **21 April 2020**
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 **SUN,Yuejian**
Facsimile No. **(86-10)62019451**	Telephone No. **010-62084097**

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2019/097014

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				KR	20120104255	A	20 September 2012
				JP	4993038	B2	08 August 2012
				JP	WO2011132490	A1	18 July 2013
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CN	107141435	A	08 September 2017	None			
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				IN	201200947	I2	26 August 2016
				IT	1407525	B	17 April 2014
JP	2003096293	A	03 April 2003	None			