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(54) Title: POLYESTER POLYOLS AND POLYURETHANES

(57) Abstract: A method for producing a polyurethane, which method comprises: - reacting (i) two dicarboxylic acids, one of which one is succinic acid, and, optionally, one or more further dicarboxylic acids; and (ii) a diol to produce a polyester polyol; and - reacting the polyester polyol and a polyisocyanate compound, thereby to produce a polyurethane



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POLYESTER POLYOLS AND POLYURETHANES

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Field of the invention

The present invention relates to a method for producing a polyurethane. The present invention also relates to a polyurethane, for example as obtainable by the method. The invention further relates to a polyester polyol suitable for the production of the polyurethane and to a product comprising and/or formed from the polyurethane.

Background to the invention

Polyurethanes are widely used because of their excellent properties and broad range of application areas. Typically, polyurethanes consist of an isocyanate and a polyol. The polyol can be a polyether polyol or a polyester polyol. In polyester polyols one may distinguish between aromatic or aliphatic polyesters.

Polyester polyols are used because they typically give better mechanical properties and better heat resistance compared to polyether polyols. Polyester polyols typically have higher hydrolysis resistance and low-temperature flexibility.

Aliphatic polyesters are used in elastomeric applications such as shoe soles applications, and in flexible foams in specialized applications such as fabric lining and in semi-rigid foams. These aliphatic polyesters are typically based on adipic acid, ethylene glycol, diethylene glycol, 1,4-butanediol, 1,6-hexanediol. Branching of the polyesters is achieved by using glycerol, trimethylolpropane or pentaerythritol. Most widely used polyesters are 2000 to 3000 molecular weight.

In recent years new renewable raw materials are being commercialized that offer new opportunities for polyester polyol and polyurethanes manufacturers. Biobased succinic acid is one of those new renewable raw materials.

However, succinic acid has less carbon atoms than adipic acid which typically leads to lower hydrolytic stability of the resulting polyurethane when the molecular weight of the polyester polyol is kept constant.

The lower hydrolytic stability of succinic acid containing polyurethanes compared to adipic acid based polyurethanes is a disadvantage in many applications as they do not meet the requirements that are set by users of polyurethanes materials. Thus, this is a hurdle for polyurethane producers and users to increase the biobased content and lower the environmental footprint of their products by using biobased succinic acid.

Alternatively, sebacic acid can be used which is also biobased. However, sebacic acid is typically more expensive than adipic acid and biobased succinic acid. This will increase costs of the raw materials for polyurethane producers and users. Accordingly, there is a need for new for polyester polyols and polyurethanes which can incorporate biobased raw materials.

Summary of the invention

The invention is based on the use of a blend of succinic acid and sebacic acid in the polyester polyol to create a co-polyester polyol. The advantage of this approach is that the price of the raw materials (a mix of sebacic acid and succinic acid) will be lower than sebacic acid, and the hydrolytic performance of the resulting polyurethane will be improved in comparison with a purely succinic acid based polyurethane. At the same time, the renewable content and environmental footprint of the resulting polyester polyol and polyurethane will be improved than a purely adipic acid based polyurethane.

The present invention is based on the observation that polyurethanes made from polyester polyols and isocyanates can be based on a mixture of two or more diacids comprising at least succinic acid and sebacic acid. Typically polyurethanes are based on adipic acid. We have shown that mixtures of succinic acid and sebacic acid can be used to replace adipic acid to achieve polyurethanes that have hydrolytic stability equal or better to those based on adipic acid.

Accordingly, the invention relates to a method for producing a polyurethane, which method comprises:

- reacting (i) two dicarboxylic acids, one of which one is succinic acid, and, optionally, one or more further dicarboxylic acids; and (ii) a diol to produce a polyester polyol; and

- reacting the polyester polyol and a polyisocyanate compound,

thereby to produce a polyurethane

The invention also provides:

- 5 - a polyurethane obtainable by a method of the invention;
- a polyurethane which at least comprises, as constituent units, a dicarboxylic acid unit, an aliphatic diol unit and a polyisocyanate unit, wherein the polyurethane comprises at least two dicarboxylic acids, one of which is succinic acid, and, optionally, one or more further dicarboxylic acids;
- 10 - a polyester polyol suitable for the production of a polyurethane, which at least comprises, as constituent units, a dicarboxylic acid unit and an aliphatic diol unit, wherein the polyester polyol comprises at least two dicarboxylic acids, one of which is succinic acid, and, optionally, one or more further dicarboxylic acids; and
- a product comprising and/or formed from a polyurethane of the invention or
- 15 obtainable by a method of the invention.

Detailed description of the invention

Throughout the present specification and the accompanying claims, the words

20 "comprise", "include" and "having" and variations such as "comprises", "comprising", "includes" and "including" are to be interpreted inclusively. That is, these words are intended to convey the possible inclusion of other elements or integers not specifically recited, where the context allows.

The articles "a" and "an" are used herein to refer to one or to more than one (i.e. to

25 one or at least one) of the grammatical object of the article. By way of example, "an element" may mean one element or more than one element.

The invention relates to a method for producing a polyurethane and to a polyurethane, optionally produced by a method of the invention.

The polyurethane is based on a combination of dicarboxylic acids, one of which

30 is succinic acid.

Accordingly, the invention relates to a method for producing a polyurethane, which method comprises:

- reacting (i) two dicarboxylic acids, one of which one is succinic acid, and, optionally, one or more further dicarboxylic acids; and (ii) a diol to produce a polyester polyol; and
- reacting the polyester polyol and a polyisocyanate compound,

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thereby to produce a polyurethane.

The two dicarboxylic acids may be succinic acid and sebacic acid.

The invention also provides:

- a polyurethane obtainable by a method of the invention;
- 10 - a polyurethane which at least comprises, as constituent units, a dicarboxylic acid unit, an aliphatic diol unit and a polyisocyanate unit, wherein the polyurethane comprises at least two dicarboxylic acids, one of which is succinic acid, and, optionally, one or more further dicarboxylic acids;
- a polyester polyol suitable for the production of a polyurethane, which at least
- 15 comprises, as constituent units and a dicarboxylic acid unit, wherein the polyester polyol comprises at least two dicarboxylic acids, one of which is succinic acid, and, optionally, one or more further dicarboxylic acids; and
- a product comprising and/or formed from a polyurethane of the invention or obtainable by a method of the invention.

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In the polyurethane and polyester polyol of the invention, succinic acid and sebacic acid may be present. That is to say, a polyurethane and polyester polyol of the the invention may comprise two types of dicarboxylic acid unit, for example the polyurethane or polyester polyol may comprise succinic acid units and sebacic acid units.

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Herein, polyurethane means a polyurethane or a polyurethaneurea unless stated otherwise restricted: these two kinds of resins have substantially the same physical properties. However, structually, a polyurethane is one produced using a short-chain polyol as a chain extender, whereas a polyurethaneurea is produced using a polyamine compound as a chain extender.

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The invention is based on a method for producing a polyurethane and a polyester polyol wherein a mixture of dicarboxylic acids is used. Two dicarboxylic acids are used in the invention, one of which is succinic acid. Optionally, one or more further dicarboxylic acids may be used.

The second dicarboxylic acid other than succinic acid may be one having from 2 to 36 carbon atoms, preferably from 8 to 12 carbon atoms. This dicarboxylic acid may be sebacic acid, azealic acid or 2,5-furandicarboxylic acid.

Preferably, succinic acid and sebacic acid are used in the invention. That is to say, in the method of the invention, a polyurethane of the invention and a polyester polyol of the invention, typically a mixture of succinic acid and sebacic acid and, optionally, one or more further dicarboxylic acids may be used.

Where two dicarboxylic acids are used, typically the second dicarboxylic acid is not adipic acid.

The succinic acid content, in terms of the total dicarboxylic acids used, may be from greater than zero to 90 mol%, such as from 10 to 75 mol%, for example 20 to 70% mol%. The remaining dicarboxylic acids content may be made up wholly of a single dicarboxylic acid other than succinic acid, for example one having from 2 to 36 carbon atoms, preferably from 8 to 12 carbon atoms, preferably sebacic acid. Alternatively, the remaining dicarboxylic acids content may be made up of a dicarboxylic acid other than succinic acid, for example one having from 2 to 36 carbon atoms, preferably from 8 to 12 carbon atoms, preferably sebacic acid, and one or more further dicarboxylic acids.

When succinic acid and sebacic acid are used the molar ratio of succinic acid to sebacic acid may be about 50:50 or about 33: 67.

As set out here, one or more additional dicarboxylic acids may be used (in addition to succinic acid and a second dicarboxylic acid, preferably sebacic acid).

Examples include aliphatic dicarboxylic acids or mixtures thereof, aromatic dicarboxylic acids or mixtures thereof, aromatic dicarboxylic acids or mixtures thereof, and mixtures of an aromatic dicarboxylic acid and an aliphatic dicarboxylic acid. Of these, aliphatic dicarboxylic acids are preferred.

Examples of the aromatic dicarboxylic acid include terephthalic acid, isophthalic acid, and the like. Examples of the derivative of an aromatic dicarboxylic acid include lower alkyl esters of an aromatic dicarboxylic acid. Specific examples of the lower alkyl ester of an aromatic dicarboxylic acid include methyl esters, ethyl esters, propyl esters, butyl esters, and the like.

Of these, terephthalic acid and isophthalic acid are preferable as the aromatic dicarboxylic acid. In addition, dimethyl terephthalate and dimethyl isophthalate are

preferable as the derivative of an aromatic dicarboxylic acid. For example, a desired aromatic polyester polyol polyurethane can be produced by using an arbitrary aromatic dicarboxylic acid as in polyesters of dimethyl terephthalate or 1,4-butanediol.

5 Examples of the aliphatic dicarboxylic acid include aliphatic dicarboxylic acids or derivatives thereof. In general, the aliphatic dicarboxylic acid preferably has a carbon number of 2 or more and not more than 40. In addition, the aliphatic dicarboxylic acid is preferably a chain or alicyclic dicarboxylic acid.

Specific examples of the chain or alicyclic dicarboxylic acid having a carbon number of 2 or more and not more than 40 include oxalic acid, succinic acid, glutaric acid, adipic acid, sebacic acid, dodecane diacid, dimer acids, cyclohexanedicarboxylic acids, and the like. Of these, from the standpoint of physical properties of an obtained polymer, the aliphatic dicarboxylic acid is preferably adipic acid.

10 In addition, a derivative of succinic acid, the second dicarboxylic acid (such as sebacic acid) and one or more additional dicarboxylic acids (if present) may be used, including lower alkyl esters, such as methyl esters, ethyl esters, propyl esters and butyl esters, cyclic acid anhydrides of the foregoing aliphatic dicarboxylic acids. Of these, a methyl ester of succinic acid, sebacic acid or a mixture thereof is preferable.

15 In the method, polyurethane and polyester polyol of the invention, a diol, such as an aliphatic diol is used. If an aliphatic diol, is used, it is typically an aliphatic or alicyclic compound having two OH groups, and examples thereof include aliphatic diols in which a lower limit value of the carbon atom number is preferably 2 or more, and an upper limit value thereof is preferably not more than 10, and more preferably not more than 6.

20 The aliphatic diol unit may be an alcohol with multiple hydroxyl groups, such as glycols.

The diol unit may be one derived from an aromatic diol and/or an aliphatic diol, and known compounds can be used. Of these, the use of an aliphatic diol is preferable.

Specific examples of a suitable diol include ethylene glycol, 1,3-propanediol, 2-methyl-1,3-propanediol, neopentyl glycol, 1,5-pentanediol, 3-methyl-1,5-pentanediol, 1,2-butanediol, 1,6-hexanediol, decamethylene glycol, 1,9-nonanediol, 1,4-butanediol, 1,4-cyclohexanedimethanol, and the like. These may be used solely or in admixture of two or more kinds thereof.

Of these, ethylene glycol, 1,4-butanediol, 1,3-propanediol, 2-methyl-1,3-propanediol and 3-methyl-1,5-pentanediol are preferable. Above all, ethylene glycol, 1,4-butanediol, and a mixture thereof are preferable; and one containing, as a main component, 1,4-butanediol or 1,4-butanediol is especially preferable.

5 The diol having a branched structure is especially preferably 2-methyl-1,3-propanediol or 3-methyl-1,5-pentanediol.

When a diol having a methylene group between the hydroxyl groups and having an even carbon number is used, the mechanical strength of the resulting polyurethane increases, and when a diol having an odd carbon number or a branched structure is
10 used, the handling properties of the polyester polyol are enhanced.

In addition to the above, examples of a diol other than the aliphatic diol, which may be mixed, include aromatic diols. Though the aromatic diol is not particularly limited so far as it is an aromatic compound having two OH groups, examples thereof include aromatic diols in which a lower limit value of the carbon number is preferably 6 or more,
15 whereas in general, an upper limit value thereof is preferably not more than 15.

Specific examples of the aromatic diol include hydroquinone, 1,5-dihydroxynaphthalene, 4,4'-dihydroxydiphenyl, bis(p-hydroxyphenyl)methane, bis(p-hydroxyphenyl)-2,2-propane, and the like. In the present invention, in general, the content of the aromatic diol in the total amount of the diols is preferably not more than
20 30 % by mole, more preferably not more than 20 % by mole, and still more preferably not more than 10 % by mole.

In addition, a polyether, both ends of which are terminated with a hydroxyl group, may be used in combination with the foregoing aliphatic diol, or may be used solely. As to the polyether, both ends of which are terminated with a hydroxyl group, in
25 general, a lower limit value of the carbon number is preferably 4 or more, and more preferably 10 or more, and in general, an upper limit value thereof is preferably not more than 1,000, more preferably not more than 200, and still more preferably not more than 100.

Specific examples of the polyether, both ends of which are terminated with a
30 hydroxyl group, include diethylene glycol, triethylene glycol, polyethylene glycol, polypropylene glycol, polytetramethylene glycol, poly-1,3-propanediol, poly-1,6-hexamethylene glycol, and the like. In addition, a copolymer polyether between polyethylene glycol and polypropylene glycol and the like can also be used.

In general, the use amount of such a polyether, both ends of which are terminated with a hydroxyl group, is a calculated amount of preferably not more than 90 % by weight, more preferably not more than 50 % by weight, and still more preferably not more than 30 % by weight as the content in the polyester.

5 In the invention, one or more of the dicarboxylic acids, i.e. the succinic acid and/or second dicarboxylic acid (such as sebacic acid) and/or optional one or more further dicarboxylic acids, and/or the diol may be derived wholly or in part from a biomass resource, i.e. it may be biobased.

10 The term "biomass resource" as used herein indicates a resource in which the energy of sunlight has been stored in the form of starches or celluloses by the photosynthesis of plants, animal bodies which have grown by eating plant bodies, and to products available by processing plant or animal bodies.

Of these, plant resources are more preferred as biomass resources. Examples include wood, paddy straws, rice husks, rice bran, long-stored rice, corn, sugarcane, 15 cassava, sago palms, bean curd refuses, corn cobs, tapioca wastes, bagasse, plant oil wastes, potatoes, buckwheats, soybeans, oils or fats, used paper, residues after paper manufacture, residues of marine products, livestock excrement, sewage sludge and leftover food. Of these, wood, paddy straws, rice husks, rice bran, long-stored rice, corn, sugarcane, cassava, sago palms, bean curd refuses, corn cobs, tapioca wastes, 20 bagasse, plant oil wastes, potatoes, buckwheats, soybeans, oils or fats, used paper, and residues after paper manufacture are preferred, with wood, paddy straws, rice husks, long-stored rice, corn, sugarcane, cassava, sago palms, potatoes, oils or fats, used paper, and residues after paper manufacture being more preferred. Corn, sugarcane, cassava and sago palms are most preferred. These biomass resources 25 typically contain a nitrogen element, and many alkali metals and alkaline earth metals such as Na, K, Mg and Ca.

These biomass resources are transformed into carbon sources after, not particularly limited to, known pretreatment and glycosylation steps such as chemical treatment with acids or alkalis, biological treatment with microorganisms and physical 30 treatment. This step typically includes, but not particularly limited to, a miniaturization step by pretreatment to make biomass resources into chips, or shave or grind them. It includes if necessary a pulverization step in a grinder or mill. The biomass resources thus miniaturized are converted into carbon sources after the pretreatment and

glycosylation-steps. Specific examples of the pretreatment and glycosylation methods include chemical methods such as treatment with a strong acid such as sulfuric acid, nitric acid, hydrochloric acid or phosphoric acid, alkali treatment, ammonia freeze explosion treatment, solvent extraction, supercritical fluid treatment and treatment with an oxidizing agent; physical methods such as fine grinding, steam explosion treatment, treatment with microwaves and exposure to electron beam; and biological treatment such as hydrolysis with microorganisms or enzymatic treatment.

As the carbon sources derived from the above-described biomass resources, typically used are fermentable carbohydrates such as hexoses such as glucose, mannose, galactose, fructose, sorbose and tagatose; pentoses such as arabinose, xylose, ribose, xylulose and ribulose; disaccharides and polysaccharides such as pentosan, saccharose, starch and cellulose; oils or fats such as butyric acid, caproic acid, caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, palmitoleic acid, stearic acid, oleic acid, linoleic acid, linolenic acid, monolauric acid, arachic acid, eicosenoic acid, arachidonic acid, behenic acid, erucic acid, docosapentaenoic acid, docosahexaenoic acid, lignoceric acid, and ceric acid; and polyalcohols such as glycerin, mannitol, xylitol and ribitol. Of these, glucose, fructose and xylose are preferred, with glucose being especially preferred. As carbon sources derived from plant resources in a broad sense, celluloses, a main component of paper, are preferred.

A dicarboxylic acid is synthesized using the above-described carbon sources in accordance with the fermentation process utilizing microbial conversion, a chemical conversion process including a reaction step such as hydrolysis, dehydration, hydration or oxidation, or a combination of the fermentation process and chemical conversion process. Of these, the fermentation process utilizing microbial conversion is preferred.

No particular limitation is imposed on the microorganism used for microbial conversion insofar as it has a producing capacity of a dicarboxylic acid.

For example, a process for recovering of succinic acid from a biomass-derived-resource may comprise fermenting a microbial cell in a fermentation broth to produce succinic acid. Fermenting a microbial cell usually comprises growth phase during which a microbial cell is grown to a desired cell density, and a production phase during which succinic acid is produced. The fermentation conditions during a growth phase and a

(succinic) production phase may be similar or different, for instance with respect to the composition of a fermentation medium, pH or temperature.

A fermentation broth may be any suitable broth allowing growth of a microbial cell and/or production of succinic acid. The fermentation broth may comprise any
5 suitable carbon source such as glucose, fructose, galactose, xylose, arabinose, sucrose, lactose, raffinose and glycerol. Fermenting a microbial cell may be carried out under aerobic conditions, anaerobic conditions, micro-aerophilic or oxygen limited conditions, or a combination of these fermentation conditions, for instance as disclosed in WO2009/083756. An anaerobic fermentation process is herein defined as a
10 fermentation process run in the absence of oxygen or in which substantially no oxygen is consumed, preferably less than 5, 2.5 or 1 mmol/L/h, and wherein organic molecules serve as both electron donor and electron acceptors.

Fermenting of a microbial cell may be carried out at any suitable pH between 1 and 9, depending on the microbial cell. In the event a microbial cell is a bacterial cell,
15 the pH in the fermentation broth preferably is between 5 and 8, preferably between 5.5 and 7.5. Usually the pH of a bacterial fermentation broth is maintained at these values by adding neutralizing agents such potassium- or sodium hydroxide, or ammonium. In the event the microbial cell is a fungal cell the pH in the fermentation broth may range between 1 and 7, preferably between 2 and 6, preferably between 2.5 and 5. The pH
20 value during a growth phase of a fungal cell may be higher than during a (succinic acid) production phase. During fermentative production of succinic acid by a fungal cell the pH value may decrease to a pH of between 1 and 4, for instance between 2 and 3, for instance between 2.5 and 3.5. The pH during a growth phase and/or a production phase during fungal fermentation may be maintained at a desired pH value by adding a
25 neutralizing agent.

A suitable temperature at which the fermenting of a microbial cell may be carried out may be between 5 and 60 degrees Celsius, preferably between 10 and 50 degrees Celsius, more preferably between 15 and 40 degrees Celsius, more preferably between 20°C and 30 degrees Celsius, depending on the microbial cell. The skilled man in the
30 art knows the optimal temperatures for fermenting a microbial cell.

In one embodiment, the microbial cell is a bacterium from the genus Mannheimia, Anaerobiospirillum, Bacillus, or Escherichia, or a fungal cell from the genus Schizosaccharomyces, Saccharomyces, Aspergillus, Penicillium, Pichia,

Kluyveromyces, Yarrowia, Candida, Hansenula, Humicola, Torulaspora, Trichosporon, Brettanomyces, Rhizopus, Zygosaccharomyces, Pachysolen, Issatchenkia or Yamadazyma. A bacterial cell may belong to a species Mannheimia succiniciproducens, Anaerobiospirillum succiniciproducens Bacillus amylophilus, B. ruminicola or E. coli, for instance an E. coli. A fungal cell may belong to a species Saccharomyces cerevisiae, Saccharomyces uvarum, Saccharomyces bayanus, Schizosaccharomyces pombe, Aspergillus niger, Penicillium chrysogenum, P. symplissicum, Pichia stipidis, Kluyveromyces marxianus, K. lactis, K. thermotolerans, Yarrowia lipolytica, Candida sonorensis, C. glabrata, Hansenula polymorpha, Torulaspora delbrueckii, Brettanomyces bruxellensis, Rhizopus orizae, Issatchenkia orientalis or Zygosaccharomyces bailii. A fungal is for instance a yeast, for instance a Saccharomyces cerevisiae.

The microbial cell may be any suitable wild-type organism, or a genetically modified microorganism. Suitable genetically modified E. coli cells are disclosed in Sanchez et al., Metabolic Engineering, 7 (2005) 229-239, WO2006/031424, and US 7,223,567. Suitable fungal cells are disclosed in WO2009/065780 and WO2009/065778.

In the present invention, diols derived from biomass resources may be used as such a diol. Specifically, the diol compound may be produced directly from carbon sources such as glucose. by the fermentation method, or a dicarboxylic acid, a dicarboxylic anhydride, or a cyclic ether, as obtained by the fermentation method, may be converted into a diol compound by a chemical reaction.

For example, 1,4-butanediol, may be produced by means of chemical synthesis of succinic acid, succinic anhydride, a succinic acid ester, maleic acid, maleic anhydride, a maleic acid ester, tetrahydrofuran, [gamma]-butyrolactone, or the like, as obtained by the fermentation method, or 1,4-butanediol may be produced from 1,3-butadiene obtained by the fermentation process. Of these, a method of obtaining 1,4-butanediol by means of hydrogenation of succinic acid in the presence of a reduction catalyst is efficient and preferable.

Examples of the catalyst to be used for hydrogenating succinic acid include Pd, Ru, Re, Rh, Ni, Cu, and Co, and compounds thereof. More specifically, examples thereof include Pd/Ag/Re, Ru/Ni/Co/ZnO, Cu/Zn oxide, Cu/Zn/Cr oxide, Ru/Re, Re/C, Ru/Sn, Ru/Pt/Sn, Pt/Re/alkali, Pt/Re, Pd/Co/Re, Cu/Si, Cu/Cr/Mn, ReO/CuO/ZnO,

CuO/CrO, Pd/Re, Ni/Co, Pd/CuO/CrO₃, Ru phosphate, Ni/Co, Co/Ru/Mn, Cu/Pd/KOH, and Cu/Cr/Zn. Of these, Ru/Sn or Ru/Pt/Sn is preferable from the standpoint of catalytic activity.

Methods for producing a diol compound from biomass resources through a combination of known organic chemical catalytic reactions are also known and may be used to provide biomass-resource derived diol for use in the invention. For example, in the case of utilizing pentose as a biomass resource, a diol such as butanediol. can be easily produced through a combination of known dehydration reaction and catalytic reaction.

Examples of the polyisocyanate compound which is used in the present invention include aromatic diisocyanates such as 2,4- or 2,6-tolylene diisocyanate, xylylene diisocyanate, 4,4'-diphenylmethane diisocyanate (MDI), p-phenylene diisocyanate, 1,5-naphthalene diisocyanate, tolidine diisocyanate; aromatic ring-containing aliphatic diisocyanates such as [alpha],[alpha],[alpha]',[alpha]'-tetramethylxylylene diisocyanate,; aliphatic diisocyanates such as methylene diisocyanate, propylene diisocyanate, lysine diisocyanate, 2,2,4- or 2,4,4-trimethylhexamethylene diisocyanate, 1,6-hexamethylene diisocyanate; alicyclic diisocyanates such as 1,4-cyclohexane diisocyanate, methylcyclohexane diisocyanate (hydrogenated TDI), 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethylcyclohexane (IPDI), 4,4'-dicyclohexylmethane diisocyanate, isopropylidenedicyclohexyl-4,4'-diisocyanate; and the like. These may be used solely or in combination of two or more kinds thereof.

In the present invention, aromatic polyisocyanates having especially high reactivity are preferable, and in particular, tolylene diisocyanate (TDI) and diphenylmethane diisocyanate (hereinafter sometimes referred to as "MDI") are preferable. In addition, polyisocyanates in which a part of NCO groups thereof is modified into urethane, urea, burette, allophanate, carbodiimide, oxazolidone, amide, imide, or the like may be used, and furthermore, polynuclear bodies include those containing an isomer other than the foregoing.

In general, a use amount of such a polyisocyanate compound is preferably from 0.1 equivalents to 10 equivalents, more preferably from 0.8 equivalents to 1.5 equivalents, and still more preferably from 0.9 equivalents to 1.05 equivalents to 1

equivalent of the hydroxyl group of the polyester polyol, and the hydroxyl group and amino group of the chain extender.

When the use amount of the polyisocyanate is not more than 10 equivalents, the matter that an unreacted isocyanate group causes an undesirable reaction is prevented, and desired physical properties are easily obtainable. In addition, when the use amount of the polyisocyanate is 0.1 equivalents or more, the molecular weights of the polyurethane and the polyurethaneurea become sufficiently large, so that desired performances can be revealed.

In the present invention, a chain exchanger having two or more active hydrogens may be used according to the need. The chain extender is classified mainly into a compound having two or more hydroxyl groups and a compound having two or more amino groups. Of these, a short-chain polyol, specifically a compound having two or more hydroxyl groups, is preferable for the polyurethane application; and a polyamide compound, specifically a compound having two or more amino groups, is preferable for the polyurethane application.

In addition, in the polyurethane resin of the present invention, when a compound having a molecular weight (number average molecular weight) of not more than 500 is used in combination as the chain extender, rubber elasticity of a polyurethane elastomer is enhanced, and hence, such is more preferable from the standpoint of physical properties.

Examples of the compound having two or more hydroxyl groups include aliphatic glycols such as ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 2,3-butanediol, 3-methyl-1,5-pentanediol, neopentyl glycol, 2-methyl-1,3-propanediol, 2-methyl-2-propyl-1,3-propanediol, 2-butyl-2-ethyl-1,3-propanediol, 1,5-pentanediol, 1,6-hexanediol, 2-methyl-2,4-pentanediol, 2,2,4-trimethyl-1,3-pentanediol, 2-ethyl-1,3-hexanediol, 2,5-dimethyl-2,5-hexanediol, 2-butyl-2-hexyl-1,3-propanediol, 1,8-octanediol, 2-methyl-1,8-octanediol, 1,9-nonanediol; alicyclic glycols such as bishydroxymethylcyclohexane; aromatic ring-containing glycols such as xylylene glycol, bishydroxyethoxybenzene; and the like.

Examples of the compound having two or more amino groups include aromatic diamines such as 2,4- or 2,6-tolylenediamine, xylylenediamine, 4,4'-diphenylmethanediamine; aliphatic diamines such as ethylenediamine, 1,2-

propylenediamine, 1,6-hexanediamine, 2,2-dimethyl-1,3-propanediamine, 2-methyl-1,5-pentanediamine, 1,3-diaminopentane, 2,2,4- or 2,4,4-trimethylhexanediamine, 2-butyl-2-ethyl-1,5-pentanediamine, 1,8-octanediamine, 1,9-nonanediamine, 1,10-decanediamine,; alicyclic diamines such as 1-amino-3-aminomethyl-3,5,5-trimethylcyclohexane (IPDA), 4,4'-dicyclohexylmethanediamine (hydrogenated MDA), isopropylidenecyclohexyl-4,4'-diamine, 1,4-diaminocyclohexane, 1,3-bisaminomethylcyclohexane.

Of these, ethylene glycol, diethylene glycol, 1,3-propanediol, 1,4-butanediol, 3-methyl-1,5-pentanediol, neopentyl glycol, 2-methyl-1,3-propanediol, isophoronediamine, hexamethylenediamine, ethylenediamine, propylenediamine, 1,3-diaminopentane, and 2-methyl-1,5-pentanediamine are preferable in the present invention.

In these chain extenders, when the aromatic polyisocyanate is used, one having a hydroxyl group is preferable, whereas when the aliphatic polyisocyanate is used, one having an amino group is preferable. In addition, these chain extenders may be used solely or in combination of two or more kinds thereof. Though a use amount of such a chain extender is not particularly limited, in general, it is preferably 0.1 equivalents or more and not more than 10 equivalents to 1 equivalent of the polyester polyol.

When the amount of the chain extender is not more than 10 equivalents, the matter that the resulting polyurethane and polyurethaneurea resins become excessively rigid is prevented, desired characteristics are obtained, and the resins are easily soluble in a solvent, so that processing is easy. In addition, when the use amount of the chain extender is 0.1 equivalents or more, the resulting polyurethane and polyurethane resins do not become excessively soft, sufficient strength and elasticity recovering performance or elasticity retaining performance are obtained, and high-temperature characteristics can be enhanced.

In addition, for the purpose of controlling the molecular weight of the polyurethane resin, a chain terminator having one active hydrogen group can be used according to the need. Examples of such a chain terminator include aliphatic monools having a hydroxyl group, such as ethanol, propanol, butanol, hexanol; and aliphatic monoamines having an amino group, such as diethylamine, dibutylamine, monoethanolamine, diethanolamine. These may be used solely or in combination of two or more kinds thereof.

In addition, for the purpose of increasing the heat resistance or strength of the polyurethane resin, a crosslinking agent having three or more active hydrogen groups can be used according to the need. Trimethylolpropane, glycerin and isocyanate modified products thereof, polymeric MDI, and the like can be used as such a crosslinking agent.

Furthermore, other additives than those described above may be added to the polyurethane resin of the present invention according to the need. Examples of such additives include antioxidants, light stabilizers, ultraviolet ray absorbers, silicone, flame retardants, colorants, hydrolysis inhibitors, fillers, lubricants, oils, surfactants, other inorganic extenders and organic solvents. In addition, a blowing agent may be added.

A polyurethane according to the present invention, or obtainable according to a method of the invention, may be any polyurethane produced from polyester polyol which is produced through a reaction of components as described herein.

A typical polyester polyol which is used for the production of a polyurethane according to the present invention may be as follows:

Examples of a polyester polyol using succinic acid and sebacic acid include a polyester polyol composed of succinic acid, sebacic acid and ethylene glycol, a polyester polyol composed of succinic acid, sebacic acid and 1,3-propylene glycol, a polyester polyol composed of succinic acid, sebacic acid and 2-methyl-1,3-propanediol, a polyester polyol composed of succinic acid, sebacic acid and 3-methyl-1,5-pentanediol, a polyester polyol composed of succinic acid, sebacic acid and neopentyl glycol, a polyester polyol composed of succinic acid, sebacic acid and 1,6-hexamethylene glycol, a polyester polyol composed of succinic acid, sebacic acid and 1,4-butanediol, a polyester polyol composed of succinic acid, sebacic acid and 1,4-cyclohexanedimethanol, and the like.

Polyester polyols of the invention may be used solely, or may be used in admixture of two or more kinds thereof. Furthermore, the polyester polymer may be used upon being mixed with a polyether polyol or a polycarbonate diol, or may be used upon being modified into a copolymer polyol.

In the case where the polyurethane reaction is carried out in the absence of a solvent, such a polyester polyol is preferably liquid at 40°C, and more preferably, a viscosity thereof at 40°C is not more than 15,000 mPa.s.

A polyester polyol according to the present invention may be prepared according to the follow description.

The succinic acid, second dicarboxylic acid (such as sebacic acid) and optionally one or more dicarboxylic acids are mixed. Each may comprise a component
5 derived from biomass resource and a component not derived from biomass resources and used as the dicarboxylic acid.

In addition, it is preferable to use ethylene glycol, diethylene glycol, 1,4-butanediol, and the like solely or in admixture as the diol unit from the standpoints of costs and performance.

10 In the present invention, in using, as a polyester polyol forming reaction raw material, the dicarboxylic acids and/or diol obtained by the foregoing method, the polyester polyol may be produced within a reaction tank in which an oxygen concentration during the polyester polyol production reaction is controlled to not more than a specified value.

15 The foregoing production reaction is defined as a reaction of from, after charging the raw materials in an esterification reaction tank, a point of time of starting temperature rising to produce a polymer having a desired viscosity in the reaction tank at ordinary pressure or under reduced pressure until subjecting the reaction tank to pressure recovery from the reduced pressure to ordinary pressure or higher.

20 As to an oxygen concentration in the reaction tank during the production reaction, though a lower limit thereof is not particularly limited, in general, it is preferably 1.0×10^{-9} % or more, and more preferably 1.0×10^{-7} % or more relative to a total volume of the reaction tank. In general, an upper limit thereof is preferably not more than 10 %, more preferably not more than 1 %, still more preferably not more than 0.1
25 % and most preferably not more than 0.01 %. When the oxygen concentration is 1.0×10^{-9} % or more, the matter that the control step becomes complicated can be prevented.

In addition, when the oxygen concentration is not more than 10 %, the matter that coloration of the polyester polyol becomes conspicuous can be prevented.

30 The amount of diol which is used at the time of producing a polyester polyol is substantially equimolar to the diol amount necessary for obtaining a polyester polyol having a desired molecular weight relative to the molar number of the dicarboxylic acids or derivatives thereof. In general, in view of the fact that distillation is revealed during

the ester condensation and/or ester exchange reaction, it is preferable to use the diol in an excessive amount by from 0.1 to 20 % by mole.

In addition, it is preferable to carry out the ester condensation and/or ester exchange reaction in the presence of an esterification catalyst. An addition timing of the esterification catalyst is not particularly limited, and the esterification catalyst may be added at the time of charging the raw materials, or it may be added after removing water to some extent or at the time of starting the pressure reduction.

Examples of the esterification catalyst include compounds containing a metal element belonging to the Group 1 to the Group 14 of the periodic table exclusive of hydrogen and carbon. Specifically, examples thereof include organic group-containing compounds such as carboxylates, alkoxy salts, organic sulfonates, β -diketonate salts, , each containing at least one metal selected from the group consisting of titanium, zirconium, tin, antimony, cerium, germanium, zinc, cobalt, manganese, iron, aluminum, magnesium, calcium, strontium, sodium, and potassium; inorganic compounds such as oxides or halides of the foregoing metals and mixtures thereof.

There may be the case where the foregoing catalyst component is contained in the polyester polyol raw material when derived from a biomass resource from the reasons described above. In that case, such a raw material may be used as it is as a metal-containing raw material without particularly purifying the raw material.

Of these, metal compounds containing titanium, zirconium, germanium, zinc, aluminum, magnesium, or calcium, and mixtures thereof are preferable. Above of all, titanium compounds, zirconium compounds, and germanium compounds are especially preferable. In addition, for the reason that when the catalyst is in a molten or dissolved state at the time of an esterification condensation reaction, the reaction rate increases, the catalyst is preferably a compound which is in a liquid form at the time of an esterification reaction or soluble in a desired polyester polyol.

As to a reaction temperature of the esterification condensation reaction and/or ester exchange reaction between the dicarboxylic acids components and the diol component, in general, a lower limit thereof is preferably 150°C or higher, and more preferably 180°C or higher, and in general, an upper limit thereof is preferably not higher than 260°C, and more preferably not higher than 250°C. A reaction atmosphere is in general an inert gas atmosphere of nitrogen, argon, or the like. In general, a

reaction pressure is preferably from ordinary pressure to 10 Torr, and more preferably from ordinary pressure to 100 Torr.

As to a reaction time, in general, a lower limit thereof is preferably 10 minutes or longer, and in general, an upper limit thereof is preferably not longer than 10 hours, and
5 more preferably not longer than 5 hours.

In addition, the esterification reaction is carried out at ordinary pressure or under reduced pressure, the timing of pressure reduction and the degree of pressure reduction are adopted chiefly in conformity with a reaction rate and a boiling point of the raw material diol, or in the case of making an azeotropic solvent coexistent, in
10 conformity with a boiling point thereof. In order to carry out a preferred stable operation, it is preferable that the reaction is carried out at ordinary pressure at the time of starting an esterification reaction, and after a progressing esterification reaction rate reaches not more than 1/2 of the initial rate, the pressure reduction is started at a preferred timing. The pressure reduction may be started either before or after the catalyst adding
15 timing.

In an industrial production method, the reaction is decided chiefly by an outflow of the distillation component, thereby determining an end point of the reaction, and an appropriate outflow depends upon a boiling point (easiness of flowing out) of the raw material polyol component. In general, the reaction end point is determined by an acid
20 number during the reaction. In addition, as the case may be, a treatment of regulating the polyester polyol so as to have a desired molecular weight (recondensation or depolymerization by the addition of the raw material diol) is added. The reaction control is determined on the basis of the acid number. In addition, in general, the reaction end point is decided in conformity with the outflow. However, after completion of the
25 reaction, an acid number of such a product is measured, and when the acid number falls outside the target standard, the esterification reaction is again carried out, thereby regulating it so as to have a desired acid number.

The acid number which is defined as the reaction end is preferably not more than 1.0, more preferably not more than 0.5, and still more preferably not more than
30 0.2. In addition, a preferred water content at the time of completion of the reaction is preferably not more than 200 ppm, more preferably not more than 100 ppm, and still more preferably not more than 50 ppm. In order to regulate appropriate acid number and water content at the time of end point, as the case may be, the reaction can also

be carried out by adding an azeotropic solvent capable of causing azeotropy with water and forming two phases and not having active hydrogen. Though this azeotropic solvent is not particularly limited so far as it has such performances, it is generally an inexpensive aromatic compound such as benzene, toluene.

5 In addition, after the polyester polyol production reaction, the polyester polyol can be stored as it is or fed for the polyurethane reaction, or after carrying out a treatment of deactivating the added catalyst, the polyester polyol can be stored or fed for the polyurethane reaction. Though a method of deactivating the added catalyst is not particularly limited, it is preferable to use a catalyst deactivating additive such as
10 phosphite trimer, and a method involving a concern that the polyester polyol structure is broken, such as a water treatment, is rather unsuitable.

The polyester polyol of the present invention may be a solid or a liquid (in a liquid state) at ordinary temperature.

In general, a molecular weight calculated from hydroxyl number of such a
15 polyester polyol of the invention is preferably from 250 to 6000. When the molecular weight is 250 or more, when formed into a polyurethane resin, satisfactory physical properties are obtainable. In addition, when the molecular weight is not more than 6000, the viscosity of the polyester polyol does not become excessively high, and handling properties may be enhanced.

20 Furthermore, in general, a molecular weight distribution of such a polyester polyol of the invention as measured by GPC (gel permeation chromatography) is preferably from 1.2 to 4.0.

The production method of a polyurethane of the present invention is a method for producing a polyurethane including at least a step of reacting an aliphatic diol and
25 succinic acid and sebacic acid and optionally one or more additional dicarboxylic acids to produce a polyester polyol; and a step of reacting the polyester polyol and a polyisocyanate compound.

An example of the production method of a biomass-resource-derived polyurethane according to the present invention is hereunder described.

30 The polyurethane of the present invention may be produced through a reaction in a bulk state, namely in the absence of a solvent, or through a reaction in a solvent having excellent solubility against the polyurethane, such as aprotic polar solvents.

An example of the production method in the copresence of an aprotic solvent is hereunder described, but the production method is not particularly limited so far as it is carried out in the copresence of an aprotic solvent. Examples of the production method include one-stage methods and two-stage methods.

5 A one-stage method is a method of reacting a biomass-resource-derived polyester polyol, a polyisocyanate compound, and a chain extender together.

A two-stage method as referred to herein is a method of first reacting a biomass-resource-derived polyester polyol and a polyisocyanate compound to prepare a prepolymer, both ends of which are terminated with an isocyanate group, and then
10 reacting the prepolymer with a chain extender (hereinafter also referred to as "isocyanate group-terminated two-stage method"). In addition, examples of the two-stage method include a method in which after preparing a prepolymer, both ends of which are terminated with a hydroxyl group, the prepolymer and a polyisocyanate are reacted.

15 Above all, the isocyanate group-terminated two-stage method goes through a step of reacting a polyester polyol with 1 equivalent or more of a polyisocyanate in advance, thereby preparing an intermediate, both ends of which are terminated with an isocyanate, corresponding to a soft segment of the polyurethane.

The two-stage method has such a characteristic feature that when the
20 prepolymer is once prepared and then reacted with the chain extender, the molecular weight of the soft segment portion is easily regulated, distinct phase separation between the soft segment and the hard segment is easily achieved, and performances as an elastomer are easily revealed.

In particular, in the case where the chain extender is a diamine, this chain
25 extender considerably differs in the reaction rate with the isocyanate group from the hydroxyl group of the polyester polyol. Therefore, it is more preferable to carry out polyurethaneurea formation by the prepolymer method.

In the one-shot method, a solvent may be used, or may not be used. In the case where a solvent is not used, the polyisocyanate component and the polyol component
30 may be stirred and mixed using a low-pressure foaming machine or a high-pressure foaming machine, or using a high-speed rotary mixer.

In the case of using a solvent, examples of the solvent include ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone; ethers such as

dioxane, tetrahydrofuran; hydrocarbons such as hexane, cyclohexane; aromatic hydrocarbons such as toluene, xylene; esters such as ethyl acetate, butyl acetate; halogenated hydrocarbons such as chlorobenzene, trichlene, perchlene; aprotic polar solvents such as [gamma]-butyrolactone, dimethyl sulfoxide, N-methyl-2-pyrrolidone, N,N-dimethylformamide, N,N-dimethylacetamide; and mixtures of two or more kinds thereof.

In the present invention, of these organic solvents, in the case of producing a polyurethane, aprotic polar solvents are preferable from the viewpoint of solubility, an aspect of which is a characteristic feature of the present invention. Furthermore, specific examples of the preferred aprotic polar solvent are exemplified. That is, methyl ethyl ketone, methyl isobutyl ketone, N,N-dimethylacetamide, N,N-dimethylformamide, N-methyl-2-pyrrolidone, and dimethyl sulfoxide are more preferable, with N,N-dimethylformamide and N,N-dimethylacetamide being especially preferable.

In the case of the one-shot method (reaction in one stage), as to an NCO/active hydrogen group (polyester polyol and chain extender) reaction equivalent ratio, in general, a lower limit thereof is preferably 0.50, and more preferably 0.8; and in general, an upper limit thereof is preferably 1.5, and more preferably 1.2.

When the reaction equivalent ratio is not more than 1.5, the matter that the excessive isocyanate groups cause side reactions to give unpreferable influences to physical properties of the polyurethane can be prevented. In addition, where the reaction equivalent ratio is 0.50 or more, the molecular weight of the resulting polyurethane sufficiently increases, and the generation of problems on strength or thermal stability can be prevented.

In general, the respective components are preferably reacted at from 0 to 100°C. It is preferable that this temperature is regulated by the amount of the solvent, reactivity of the raw materials used, reaction equipment, and the like. Too low temperatures are undesirable because the reaction proceeds too slowly, and the raw materials and polymerization product have low solubility, resulting in poor productivity. In addition, too high temperatures are undesirable because side reactions and decomposition of the polyurethane resin occur. The reaction may be carried out under reduced pressure while degassing.

In addition, a catalyst, a stabilizer, or the like may be added for the reaction according to the need.

In the two-stage method, in general, the polyisocyanate component and the polyol ingredient are reacted in a reaction equivalent ratio of preferably from 1.0 to 10.00 in advance, thereby producing a prepolymer. Subsequently, a polyisocyanate component and an active hydrogen compound component such as a polyhydric alcohol, an amine compound are added to the prepolymer, thereby carrying out a two-stage reaction. In particular, a method in which the polyol component is reacted with a polyisocyanate compound in an amount of at least one equivalent to the polyol ingredient to form a prepolymer, both ends of which are terminated with NCO, and a short-chain diol or a diamine that is a chain extender is then allowed to act on the prepolymer to obtain a polyurethane, is useful.

In the two-stage method, a solvent may be used, or may not be used. In the case of using a solvent, examples of the solvent include ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone; ethers such as dioxane, tetrahydrofuran; hydrocarbons such as hexane, cyclohexane; aromatic hydrocarbons such as toluene, xylene; esters such as ethyl acetate, butyl acetate; halogenated hydrocarbons such as chlorobenzene, trichlene, perchlene; aprotic polar solvents such as [gamma]-butyrolactone, dimethyl sulfoxide, N-methyl-2-pyrrolidone, N,N-dimethylformamide, N,N-dimethylacetamide; and mixtures of two or more kinds thereof.

In synthesizing a prepolymer terminated with an isocyanate group, any of the following methods may be used: (1) a polyisocyanate compound is first reacted directly with the polyester polyol without using a solvent, to synthesize a prepolymer, and this prepolymer is used as it is; (2) a prepolymer is synthesized by the method (1) and then dissolved in a solvent, followed by providing for the use; and (3) a solvent is used from the beginning to react a polyisocyanate and a glycol.

In the case of the method (1), it is important in the present invention that a polyurethane is obtained in the state of coexisting with a solvent by a method in which in allowing a chain extender to act, the chain extender is dissolved in a solvent, or the prepolymer and the chain extender are simultaneously introduced into a solvent, or the like.

As to an NCO/active hydrogen group (polyester polyol) reaction equivalent ratio, in general, a lower limit thereof is preferably 1, and more preferably 1.1; and in general, an upper limit thereof is preferably 10, more preferably 5, and still more preferably 3.

A use amount of the chain extender is not particularly limited. In general, a lower limit thereof is preferably 0.8, and more preferably 1, and in general, an upper limit thereof is preferably 2, and more preferably 1.2, relative to the equivalent of the NCO group contained in the prepolymer.

5 When the foregoing ratio is not more than 2, the matter that the excessive isocyanate groups cause side reactions to give unpreferable influences to physical properties of the polyurethane can be prevented. In addition, where the foregoing ratio is 0.8 or more, the molecular weight of the resulting polyurethane sufficiently increases, and the generation of problems on strength or thermal stability can be prevented.

10 In addition, a monofunctional organic amine or alcohol may be allowed to coexist at the time of reaction.

In general, the respective components are reacted preferably at from 0 to 250°C. It is preferable that this temperature is regulated by the amount of the solvent, reactivity of the raw materials used, reaction equipment, and the like. Too low
15 temperatures are undesirable because the reaction proceeds too slowly, and the raw materials and polymerization product have low solubility, resulting in poor productivity. In addition, too high temperatures are undesirable because side reactions and decomposition of the polyurethane resin occur. The reaction may be carried out under reduced pressure while degassing.

20 In addition, a catalyst, a stabilizer, or the like may be added for the reaction according to the need.

At the time of polyurethane production of the present invention, in the case of adding a crosslinking agent for an application requiring heat resistance or strength, it is preferable to make its addition amount larger than that at the time of using a generally
25 used petroleum-derived dicarboxylic acid. In addition, since the viscosity of the polyurethane obtained at the time of polyurethane production of the present invention is low, at the time of post-treatment and processing of the polyurethane, it is preferable to make the temperature slightly lower than that at the time of using petroleum-derived succinic acid, resulting in favorable handling properties, stability and economy.

30 Polyurethane materials and applications exist in many different forms, such as foams (rigid and flexible), micro-cellular elastomers (porous), compact elastomers (i.e. non-porous), coatings.

Generally speaking, polyurethane elastomers have excellent mechanical properties, including elasticity, resilience and abrasion resistance.

In addition to that, the so-called microcellular polyurethanes allow for strongly reduced densities, commonly in the range of 0.4 to 0.7 g/cm³, compared to a density of approximately 1.2 g/cm³ for non-porous polyurethanes.

Thermoplastic polyurethanes (TPUs) represent another sub-class of the group of polyurethane elastomers. TPUs are thermoplastic elastomers consisting of linear molecular chains, as opposed to thermosetting polyurethanes, that have a 3-dimensionally cross-linked structure. The linear chains in a TPU are composed of both hard segments (isocyanate rich) and soft segments (polyol rich); these hard and soft segments are arranged in a block structure. The high polarity in the hard segments creates a strong intermolecular interaction, leading to quasi-crystalline areas. These quasi crystalline areas act as physical cross-links between the molecules, which despite the linear molecules give it an elastomeric character with high elasticity. These physical crosslinks are "broken" when the material is heated, causing the material to become liquid and making it suitable for the classical polymer processes such as extrusion and injection molding.

The polyurethane and urethane prepolymer solution thereof as produced by the present invention can reveal a variety of characteristics and can be widely used as foams, elastomers, coating materials, fibers, adhesives, flooring materials, sealants, medical materials, artificial leathers, and the like.

The polyurethane, polyurethaneurea, and urethane prepolymer solution thereof as produced by the present invention are also usable as a casting polyurethane elastomer. Examples thereof include rolls such as rolling rolls, papermaking rolls, business appliances, pretensioning rolls; solid tires, casters, or the like for fork lift trucks, automotive vehicle newtrams, carriages, carriers, and the like; and industrial products such as conveyor belt idlers, guide rolls, pulleys, steel pipe linings, rubber screens for ore, gears, connection rings, liners, impellers for pumps, cyclone cones, cyclone liners. In addition, the polyurethane, polyurethaneurea, and urethane prepolymer solution thereof are applicable to belts for OA apparatus, paper feed rolls, squeegees, cleaning blades for copying, snowplows, toothed belts, surf rollers, and the like.

The polyurethane and urethane prepolymer solution thereof as produced by the present invention are also applicable to an application as thermoplastic elastomers. For example, the polyurethane and the urethane prepolymer solution can be used as tubes or hoses in pneumatic apparatus for use in the food and medical fields, coating apparatus, analytical instruments, physicochemical apparatus, constant delivery pumps, water treatment apparatus, industrial robots, and the like and as spiral tubes, hoses for firefighting. In addition, the polyurethane and the urethane prepolymer solution are usable as belts such as round belts, V-belts, flat belts. in various transmission mechanisms, spinning machines, packaging apparatus, printing machines, and the like.

In addition, examples of elastomer applications include heel tops of footwear, shoe soles, apparatus parts such as cup rings, packings, ball joints, bushings, gears, rolls, sports goods, leisure goods, belts of wristwatches, and the like.

Furthermore, examples of automotive parts include oil stoppers, gear boxes, spacers, chassis parts, interior trims, tire chain substitutes, and the like. In addition, examples thereof include films such as key board films, automotive films, curl cords, cable sheaths, bellows, conveying belts, flexible containers, binders, synthetic leathers, dipping products, adhesives, and the like.

The polyurethane and urethane prepolymer solution thereof as produced by the present invention are also applicable to an application as a solvent based two-pack type coating material and can be applied to wood products such as musical instruments, family Buddhist altars, furniture, decorative plywood, sports goods. In addition, the polyurethane and urethane prepolymer solution are also usable as a tar-epoxy-urethane for automotive vehicle repair.

The polyurethane and urethane prepolymer solution thereof as produced by the present invention are usable as a component of moisture-curable one-pack type coating materials, block isocyanate type solvent coating materials, alkyd resin coating materials, urethane-modified synthetic resin coating materials, ultraviolet ray-curable coating materials, and the like.

Such coating materials can be used, for example, as coating materials for plastic bumpers, strippable paints, coating materials for magnetic tapes, overprint varnishes for floor tiles, flooring materials, paper, woodgrained films, and the like, varnishes for wood, coil coatings for high processing, optical fiber protection coatings,

solder resists, topcoats for metal printing, base coats for vapor deposition, white coats for food cans, and the like.

The polyurethane and urethane prepolymer solution thereof as produced by the present invention are applicable as an adhesive to shoes, footwear, magnetic tape
5 binders, decorative papers, wood, structural members, and the like. In addition, the polyurethane and urethane prepolymer solution can be used also as a component of adhesives for low-temperature use and hot-melt adhesives.

The polyurethane and urethane prepolymer solution thereof as produced by the present invention are usable as a binder in applications such as magnetic recording
10 media, inks, castings, burned bricks, grafting materials, microcapsules, granular fertilizers, granular agricultural chemicals, polymer cement mortars, resin mortars, rubber chip binders, reclaimed foams, glass fiber sizing, and the like.

The polyurethane and urethane prepolymer solution thereof as produced by the present invention are usable as a component of fiber processing agents for shrink
15 proofing, crease proofing, water repellent finishing, and the like.

The polyurethane, polyurethaneurea, and urethane prepolymer solution thereof as produced by the present invention are applicable as a sealant/caulking material to walls formed by concrete placing, induced joints, the periphery of sashes, wall type PC joints, ALC joints, and joints of boards and as a sealant for composite glasses, sealant
20 for heat-insulating sashes, sealant for automotive vehicles, and the like.

The polyurethane produced by the present invention is suitable for applications to polyurethanes for shoe sole, synthetic leathers, and artificial leathers. In addition, at the time of using the polyurethane produced by the present invention, the polyester polyol component may have a skeleton of adipic acid, sebacic acid, or the like.
25 Furthermore, since such a polyurethane of the present invention is derived from plants and is biodegradable, it is further suitable for non-durable consumer goods such as resins for shoe.

A reference herein to a patent document or other matter which is given as prior art is not to be taken as an admission that that document or matter was known or that
30 the information it contains was part of the common general knowledge as at the priority date of any of the claims.

The disclosure of each reference set forth herein is incorporated herein by reference in its entirety.

Embodiments of the invention:

1. A method for producing a polyurethane, which method comprises:

- reacting (i) two dicarboxylic acids, one of which one is succinic acid, and, optionally, one or more further dicarboxylic acids; and (ii) a diol to produce a polyester polyol; and
- reacting the polyester polyol and a polyisocyanate compound,

thereby to produce a polyurethane.

2. A method according to embodiment 1, wherein the two dicarboxylic acids are succinic acid and a dicarboxylic acid having from 2 to 36 carbon atoms, preferably from 8 to 12 carbon atoms.

3. A method according to embodiment 1 or 2, wherein the two dicarboxylic acids are succinic acid and sebacic acid.

4. A method according to embodiment 1 or 2, wherein the two dicarboxylic acids are succinic acid and azealic acid or 2,5-furandicarboxylic acid.

5. A method according to any one of the preceding embodiments, wherein the succinic acid content of the total dicarboxylic acids used is from greater than zero to 90 mol%.

6. A method according to any one of the preceding embodiments, wherein at least part of the two dicarboxylic acids or one or more further dicarboxylic acids is derived from a biomass resource.

7. A method according to any one of the preceding embodiments, wherein at least part of the succinic acid is derived from a biomass resource.

8. A polyurethane obtainable by a method according to any one of the preceding embodiments.

5 9. A polyurethane which at least comprises, as constituent units, a dicarboxylic acid unit, an aliphatic diol unit and a polyisocyanate unit, wherein the polyurethane comprises at least two dicarboxylic acids, one of which is succinic acid, and, optionally, one or more further dicarboxylic acids.

10 10. A polyurethane according to embodiment 9, wherein the two dicarboxylic acids are succinic acid and a dicarboxylic acid having from 2 to 36 carbon atoms, preferably from 8 to 12 carbon atoms.

15 11. A polyurethane according to embodiment 9 or 10, wherein the two dicarboxylic acids are succinic acid and sebacic acid.

12. A polyurethane according to embodiment 9 or 10, wherein the two dicarboxylic acids are succinic acid and azealic acid or 2,5-furandicarboxylic acid.

20 13. A polyurethane according to any one of embodiments 9 to 12, wherein the succinic acid content of the total dicarboxylic acids content is from greater than zero to 90 mol%.

25 14. A polyurethane according to any one of embodiments 9 to 13, wherein at least part of the two dicarboxylic acids or one or more further dicarboxylic acids is derived from a biomass resource.

15. A polyurethane according to any one of embodiments 9 to 14, wherein at least part of the succinic acid is derived from a biomass resource.

30 16. A polyurethane according to any one of embodiments 9 to 15, wherein the aliphatic diol unit is an alcohol with multiple hydroxyl groups, such as glycols.

17. A polyurethane according to any one of embodiments 9 to 16, wherein the aliphatic diol unit is an ethylene glycol unit, a 1,4-butanediol unit, a di-ethyleneglycol unit or a 1,6-hexanediol unit.

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18. A polyurethane according to any one of embodiments 9 to 17, retaining preferably 70%, more preferably 75 % of its mechanical properties after conditioning for 7 days at 70° C and 95 % relative humidity RH.

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19. A polyester polyol suitable for the production of a polyurethane, which at least comprises, as constituent units, a dicarboxylic acid unit and an aliphatic diol unit, wherein the polyester polyol comprises at least two dicarboxylic acids, one of which is succinic acid, and, optionally, one or more further dicarboxylic acids.

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20. A polyester polyol according to embodiment 19, having a number average molecular weight of from about 250 g/mol to about 6000 g/mol.

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21. A polyester polyol according to embodiment 19 or 20, wherein the two dicarboxylic acids are succinic acid and a dicarboxylic acid having from 2 to 36 carbon atoms, preferably from 8 to 12 carbon atoms.

22. A polyester polyol according to any one of embodiments 19 to 21, wherein the two dicarboxylic acids are succinic acid and sebacic acid.

25

23. A polyester polyol according to any one of embodiments 19 to 21, wherein the two dicarboxylic acids are succinic acid and azealic acid or 2,5-furandicarboxylic acid.

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24. A polyester polyol according to any one of embodiments 19 to 23, wherein the succinic acid content of the total dicarboxylic acids content is from greater than zero to 90 mol%.

25. A polyester polyol according to any one of embodiments 19 to 24, wherein at

least part of the two dicarboxylic acids or one or more further dicarboxylic acids is derived from a biomass resource.

26. A polyester polyol according to any one of embodiments 19 to 25, wherein at least part of the succinic acid is derived from a biomass resource.

27. A product comprising and/or formed from a polyurethane according to any one of embodiments 8 to 18.

The present invention is further illustrated by the following Examples:

EXAMPLES

Example 1: Synthesis of polyester polyols

Polyester polyols of 2000 MW were prepared following the protocol described by Sonnenschein *et al.* ("Comparison of adipate and succinate polyesters in thermoplastic polyurethanes" Polymer 51 (2010) 3685-3692).

The synthesis of polyols was carried out in a reaction kettle of 2000 ml, equipped with Dean-Stark adapter for water condensation, heating mantle, thermo couple, temperature controller and mechanical mixer with two mixing parts. The reactor has also inlet - outlet attachment for nitrogen (to provide nitrogen blanket). The flow of nitrogen was controlled with flow-meter.

Typically, the synthesis of polyester polyols was carried out according to the following procedure: calculated amount of diol(s) and diacid(s) are charged to reaction flask and heated up to 120°C. At this temperature the reaction mixture is in liquid phase and homogenized with stirring (Step-0). Calculated amount of catalyst dissolved in diol-coreactant is charged into the reaction mixture and homogenized. The temperature of reaction mixture is gradually increased from 120°C to 170°C during 3-4 hours (Step-1). In Step-1, the reaction takes place as indicated with significant (rapid) water release. Afterwards, in Step-2, the reaction temperature is increased to 180°C and carried out at this temperature for minimum 16 hours. The acid number is determined at the

completion of Step-2. At the completion of Step-2, water is present in the reaction mixture as determined by Karl Fisher titration. In the next step of synthesis (Step-3), the reaction mixture is cooled down to 120°C and de-moisturized under vacuum (<10 mmHg) for couple of hours. In Step-4, the reaction mixture is heated again to 180°C and reaction continued at this temperature to completion.

Acid number was checked at several points during polyester polyol synthesis. The amount of water released during synthesis was also measured.

Formulations and quantities of components used in preparation of polyols as well as polyol properties are shown in Table 1.

Example 2: Testing of polyols

The following properties of polyols were tested:

Method:	Property:
ASTM D 4662-08	Acid Value, mg KOH/g
ASTM D 4274-05	Hydroxyl Value, mg KOH/g
ASTM D 4672-00	Moisture, %
ASTM D 4878-08	Viscosity @70°C, cPs
ASTM D 4890-03	Color, Gardner scale and Apha scale
DSC analysis	Glass transition temperature (T _g) and melt temperature (T _m)

The results are set out in Table 1.

Table 1. Formulations and Properties of Polyester Polyols

Polyol Designation	BS-2000	BA-2000	BSC-2000	BSCSA-90/10-2000	BSCSA-80/20-2000	BSCSA-50/50-2000	BSCSA-33/67-2000
Formulation, pbw (moles)							
Adipic Acid	-	1070.5 (7.33)	-	-	-	-	-
Sebacic acid	-	-	996.4 (4.93)	924.0 (4.57)	846.4 (4.19)	582.5 (2.88)	404.1 (2.00)
Succinic Acid	1000 (8.47)	-	-	59.9 (0.51)	123.5 (1.05)	340.2 (2.88)	479.1 (4.06)
1,4-Butane diol	855 (9.5)	729.4 (8.09)	503.6 (5.59)	516.7 (5.74)	530.4 (5.89)	577.3 (6.41)	602.8 (6.69)

Butyltintris(2-ethylhexanoate)	0.07	0.127	0.1058	0.1058	0.1058	0.1058	0.1058
Diol/di-acid equivalent ratio		1.124	1.154	1.150	1.144	1.132	1.124
Acid Value, mg KOH/g	1.92	0.75	0.85	0.95	0.97	0.81	0.65
Hydroxyl Value, mgKOH/g**	59.7	57.0	56.2	57.0	56.4	57.1	56.8
Melt Temperature, °C							
-beginning of melting	99	41.85	56.56	42.92	33.86	30.10	66.83
-peak of melting	108	54.53	62.67	58.08	56.28	42.37	83.38

Example 3: Preparation of thermoplastic polyurethanes (TPUs) via One-shot

Method

TPUs were prepared via one-shot method by reacting MDI and a mixture composed of polyester polyol and a chain extender (Table below).

Sheets and round bottom samples were prepared to test physico-mechanical properties of the TPUs. The sheets were prepared using a laboratory compression molding method (Carver press). Degassed preheated polyol and a chain extender weighed into Speed Mixer cup were mixed for 30 seconds at 2200 rpm using Speed Mixer (Flack Tek Inc.) and subsequently heated for 15 minutes in an air-circulating oven at 120°C. Liquid isocyanate conditioned at 80°C was added via syringe to the mixture of polyol and the chain extender. All components were mixed via Speed Mixer at 2200 rpm and transferred into an aluminum mold covered with Teflon sheet that was preheated at 120°C. At the gel time, the mold was closed and TPU was cured for 2 hours at 120°C. Afterwards, the samples were post-cured for 16 hours at 100°C.

Formulations and quantities of components used in preparation of TPUs as well as TPU properties are shown in Table 2.

Example 4: Testing of TPUs

The following properties were measured on TPUs:

- Hardness, ASTM D-2240, Shore A and Shore D
- Tensile properties (Tensile Strength and Elongation), ASTM D 412
- Tear Strength, Dye C, ASTM D 6240

- Abrasion Resistance, ASTM D 1044 (H22 wheels, weight load 500g, 2000 cycles)
- Resilience (Bashore rebound), ASTM D2632
- Compression set, ASTM D 395
- 5 • Differential Scanning Calorimetry (DSC): (DSC Q 10, TA Instruments)
- Dynamic-mechanical analysis, DMA; (DMA 2980, TA Instruments)
- Thermo-mechanical analysis (TMA): (TMA Q400, TA Instruments)
- Heat resistance of TPUs: tensile strength and elongation at 50° and 70°C was measured by using heat chamber attached to the Instron
- 10 tester.
- Hydrolytic stability of TPUs: retention of tensile strength was determined on samples that were exposed for 7 days to 70°C and 95% RH.
- FTIR analysis: FTIR Spectrometer (Spectrum Two, Perkin Elmer with Pike Miracle ATR Attachment).

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The results are set out in Tables 1 and 3.

Table 2: Formulations and properties of TPUs

TPU designation	BA-2000	BS-2000	BSC-2000	BSCSA-90/10-2000	BSCSA-80/20-2000	BSCSA-50/50-2000	BSCSA-33/67-2000
Formulation, pbw							
BS2000, g	-	45	-	-	-	-	-
BA2000, g	54.50	-	-	-	-	-	-
BSC2000, g	-	-	54.57	-	-	-	-
BSCSA-90/10-2000, g	-	-	-	54.50	-	-	-
BSCSA-80/20-2000, g	-	-	-	-	54.56	-	-
BSCSA-50/50-2000, g	-	-	-	-	-	54.50	-
BSCSA-33/67-2000, g	-	-	-	-	-	-	54.52
4,4'-MDI, g	22.66	18.673	22.38	22.66	22.45	22.69	22.59
1,4 – BD, g	5.50	4.402	5.43	5.50	5.44	5.50	5.48
Hard segment concentration, %	34.1	34	33.8	34.1	33.8	34.1	34.0
Temp. of polyol and 1,4-BD, °C	90	120	90	80	100	100	90
Temp. of Mondur M, °C	80	80	80	80	80	80	80
Mixing via Speed mixer @ 2200RPM, s	30	20	30	30	30	30	30
Curing time and temperature	2 hrs @ 120 °C	2 hrs @ 120 °C	2 hrs @ 120 °C	2 hrs @ 120 °C	2 hrs @ 120 °C	2 hrs @ 120 °C	2 hrs @ 120 °C
Post-curing time and temperature	20 hrs @100 °C	20 hrs @100 °C	20 hrs @100 °C	20 hrs @100 °C	20 hrs @100 °C	20 hrs @100 °C	20 hrs @100 °C
Hardness @ RT							
Shore A (Sh. A)	87 (Sh. A)	-	96 (Sh. A)	95 (Sh. A)	92 (Sh. A)	90 (Sh. A)	95 (Sh. A)
Shore D (Sh. D)	38 (Sh. D)	57 (Sh. D)	47 (Sh. D)	44 (Sh. D)	42 (Sh. D)	37 (Sh. D)	44 (Sh. D)
Hardness @ RT after 6 weeks							
Shore A (Sh. A)	88 (Sh. A)	-	96 (Sh. A)	95 (Sh. A)	93 (Sh. A)	92 (Sh. A)	95 (Sh. A)
	38 (Sh. D)	-	48 (Sh. D)	45 (Sh. D)	44 (Sh. D)	38 (Sh. D)	45 (Sh. D)

Shore D (Sh. D)							
Resilience, %	44	18	46	37	47	48	41
Tensile Strength at break at RT, psi	5593.7 ± 177	6546 ± 281	4747.1 ± 259	3003.50 ± 292	4481.60 ± 77	5720.38 ± 165	5348.63 ± 303
Elongation at break at RT, %	685.15 ± 14.31	685 ± 20	564.41 ± 27	721.55 ± 42	756.20 ± 45.04	780.93 ± 18	743.11 ± 37
Max. Tear Strength – Die C, N/cm	1343.52 ± 154	1441 ± 140	1327.52 ± 105	1397 ± 31	1368.03 ± 65	1330.23 ± 68	1491.19 ± 110
Constant Deflection Compression Set, C _b , %	15.59 ± 1.01	ND	11.56 ± 1.11	16.91 ± 0.2	16.26 ± 1.25	15.46 ± 1.75	18.43 ± 2.59
Taber Abrader Test Weight Loss, mg	3.9	57	4.3	18.2	15.7	2.7	2.1
Tensile Strength at break at 50° C, psi	1913.20 ± 52	>4238	2066.04 ± 76	1582.10 ± 81	1701.93 ± 29.65	1792.29 ± 27	1667.29 ± 58
Elongation at break at 50° C, %	420.70 ± 6.43	>538	410.74 ± 5.56	438 ± 7	435.18 ± 5.93	439.39 ± 2.75	426.13 ± 6.13
Tensile Strength at break at 70° C, psi	1410.84 ± 43	>3365	1579.18 ± 69	1167 ± 70	1419.31 ± 55.61	1451.36 ± 31	1285.06 ± 56
Elongation at break at 70° C, %	420.58 ± 7.32	>538	411.44 ± 8.43	429 ± 5	446.05 ± 6.56	441.08 ± 2.16	431.78 ± 6.14
Transition temperatures via DSC	-37°C, 66°C, 163°C	-17.9°C, 80.7°C, 190°C	-39°C, 39°C, 177°C	-32°C, 38°C, 175°C	-32°C, 33°C, 168°C	-37°C, 32°C, 163°C	-34°C, 45°C, 163°C
Maximum of Loss modulus via DMA	-24°C	11.2°C	-13°C	-18°C	-4°C	-24°C	—

Table 3: Hydrolytic Stability of TPUs (Aging for 7 days at 70°C and 95% RH)

Designation	1	2	3	4	5	6
TPU Designation	BA-2000	BSC-2000	BSCSA-90/10- 2000	BSCSA-80/20- 2000	BSCSA-50/50- 2000	BSCSA-33/67- 2000
Weight gain after aging, %	0.822	1.135	0.652	0.847	1.875	1.090
Initial Tensile Strength at break, psi	5593.7 ± 177	4747.1 ± 259	3003.50 ± 292	4481.60 ± 378	5720.38 ± 165	5348.63 ± 303
Initial Elongation at break, %	685.15 ± 14.31	564.41 ± 27	721.55 ± 42	756.20 ± 45	780.93 ± 18	743.11 ± 37
Tensile Strength at break after aging, psi	4190.30 ± 315	4639.63 ± 319	2255.63 ± 141	3325.35 ± 201	4130.79 ± 209	4274.84 ± 135
Elongation at break after aging, %	724.71 ± 17	599.82 ± 11	755.22 ± 13	791.32 ± 12	846.06 ± 37	787.57 ± 13
Retention of Tensile Strength at break, psi	75 %	98 %	75.1 %	74.2 %	72 %	80 %

CLAIMS

- 5 1. A thermoplastic polyurethane elastomer which at least comprises, as constituent units, a dicarboxylic acid unit, an aliphatic diol unit and a polyisocyanate unit, wherein the thermoplastic polyurethane elastomer comprises at least two dicarboxylic acids, wherein the two dicarboxylic acids are succinic acid and a dicarboxylic acid having from 8 to 36 carbon atoms.
- 10 2. A thermoplastic polyurethane elastomer according to claim 1, wherein the two dicarboxylic acids are succinic acid and a dicarboxylic acid having from 8 to 12 carbon atoms.
- 15 3. A thermoplastic polyurethane elastomer according to claim 1 or 2, wherein the two dicarboxylic acids are succinic acid and sebacic acid.
4. A thermoplastic polyurethane elastomer according to claim 1 or 2, wherein the two dicarboxylic acids are succinic acid and azealic acid.
- 20 5. A thermoplastic polyurethane elastomer according to any one of claims 1 to 4, comprising one or more further dicarboxylic acids.
6. A thermoplastic polyurethane elastomer according to any one of claims 1 to 5, wherein at least part of the two dicarboxylic acids is derived from a biomass resource.
- 25 7. A thermoplastic polyurethane elastomer according to any one of claims 1 to 6, wherein at least part of the succinic acid is derived from a biomass resource.
- 30 8. A thermoplastic polyurethane elastomer according to any one of claims 5 to 7, wherein at least part of the one or more further dicarboxylic acids is derived from a biomass resource.

9. A thermoplastic polyurethane elastomer according to any one of claims 1 to 8, wherein the succinic acid content of the total dicarboxylic acids content is from greater than zero to 90 mol%.

5 10. A thermoplastic polyurethane elastomer according to any one of claims 1 to 9, wherein the aliphatic diol unit is an alcohol with multiple hydroxyl groups.

11. A thermoplastic polyurethane elastomer according to any one of claims 1 to 10, wherein the aliphatic diol unit is an ethylene glycol unit, a 1,4-butanediol unit, a di-
10 ethyleneglycol unit or a 1,6-hexanediol unit.

12. A thermoplastic polyurethane elastomer according to any one of claims 1 to 11, retaining at least 70% of its hydrolytic stability after conditioning for 7 days at 70° C and 95 % relative humidity RH.

15 13. A thermoplastic polyurethane elastomer according to claim 12, retaining at least 75% of its hydrolytic stability after conditioning for 7 days at 70° C and 95 % relative humidity RH.

20 14. A method for producing the thermoplastic polyurethane elastomer according to any one of claims 1 to 13, which method comprises:

- reacting (i) the two dicarboxylic acids; and, optionally, one or more further dicarboxylic acids; and (ii) the aliphatic diol to produce a polyester polyol; and

- reacting the polyester polyol and the polyisocyanate compound,

25 thereby to produce the thermoplastic polyurethane elastomer.

15. A product comprising and/or formed from a thermoplastic polyurethane elastomer according to any one of claims 1 to 13.

30 16. A product according to claim 15, wherein the product is selected from the group consisting of heel tops of footwear; shoe soles; apparatus parts such as cup rings, packings, ball joints, bushings, gears, rolls, sports goods, leisure goods, belts of

wristwatches; automotive parts including oil stoppers, gear boxes, spacers, chassis parts, interior trims, tire chain substitutes, films such as key board films, automotive films, curl cords, cable sheaths, bellows, conveying belts, flexible containers, binders, synthetic leathers, dipping products, adhesives.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/062615

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G18/66 C09D175/04 C08G18/76 C08G63/16 C08G18/42
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08G C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	abstract	1-16
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Further documents are listed in the continuation of Box C.



See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search

27 August 2015

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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