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(54) Title: UNSATURATED POLYMERS

(57) Abstract: The present invention relates to an unsaturated polyester polyol having at least 2 hydroxyl groups and a hydroxyl value of 11 to 225 mgKOH/g which is the reaction product of at least one dicarboxylic acid and at least one polyol, wherein at least one of the acid and polyol comprises dimer fatty acid and/or dimer fatty diol. The unsaturated polyester polyol is particularly suitable for reacting with polyisocyanates to form polyurethanes.



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Unsaturated Polymers

Field of Invention

The present invention relates to unsaturated polymers containing dimer residues, and in particular to an unsaturated polyester polyol, and to the use thereof as a building block for polymers, particularly polyurethanes in coating, elastomer and thermoplastic applications.

Background

Polyurethanes are very versatile materials that can be used in a variety of applications, for example elastomers, foams, coatings, adhesives, thermoplastic polyurethanes, polyurethane dispersions for coatings, dispersion of powders and textiles. Polyurethanes are formed from the reaction of a polyol with an isocyanate. There are two main types of polyol currently used in the industry i.e. polyether polyols and polyester polyols, both saturated products. Unsaturated polyols such as polybutadiene diol have also been used in polyurethanes, but here the unsaturation can result in poor resistance against UV light.

The polyurethanes, once formed can subsequently undergo a chemical reaction of the urethane functional groups with moisture to form a crosslinked material which has different properties depending on its application area. These polyurethanes have a single type of curing site i.e. the urethane functional group. Polyurethanes can also be non-reactive, meaning that they do not need (moisture) curing after application.

Application areas include polyurethane hot melt adhesives for lamination, 2-pack polyurethane adhesives for flooring, assembly, packaging etc., polyurethane sealants in cars, protective coatings, industrial coatings, wood coatings and adhesives, flooring, furniture foams, insulation, elastomer shoe soling, roller blading wheels etc.

Product properties such as toughness and flexibility can be broadly adjusted, for example by choice of polyol type(s) and ratio of polyols and isocyanate.

Polyurethanes derived from saturated polyester polyols have good adhesion properties to various substrates, lower flexibility than polyether based polyurethanes, good thermo-oxidative stability but lower hydrolysis resistance.

5 Hydroxyl containing (meth)acrylic monomers can be polymerised/copolymerised with vinyl and acrylic monomers to form an intermediate polymer. Reaction of the hydroxyl groups of the intermediate polymer with polyisocyanate forms a polyurethane with dual curing sites i.e. the urethane functional group (isocyanate) and the (meth)acrylate unsaturation which can be cured by reaction with moisture
10 and UV light respectively. These materials have different properties to those where there is only a single curing point, such as improved green strength, increased adhesion and higher shear adhesion failure temperature, higher coating hardness, increased modulus and toughness of coatings, adhesives, elastomers and foams. Also, the application viscosity can be lower. One disadvantage of this route to a
15 polyurethane with dual curing sites is that before curing takes place there will be free residual acrylic monomers present. These monomers are volatile and precautions need to be taken to handle them safely. Acrylic monomers are known to cause irritation to skin, eyes, nose throat and respiratory tract.

20 **Summary of the Invention**

We have now discovered an unsaturated polyester polyol and use thereof in a range of polymer applications which reduces or substantially overcomes at least one of the aforementioned problems.

25

Accordingly, the present invention provides an unsaturated polyester polyol comprising at least 2 hydroxyl groups has a hydroxyl value of 11 to 225 mgKOH/g and comprises the reaction product of at least one dicarboxylic acid and at least one polyol, wherein at least one of the acid and polyol comprises dimer fatty acid and/or
30 dimer fatty diol.

The invention also provides a process for preparing an unsaturated polyester polyol having a hydroxyl value of 11 to 225 mgKOH/g which comprises reacting at least one dicarboxylic acid and at least one polyol at a molar ratio in the range from

1:1.01 to 5.0, wherein at least one of the acid and polyol comprises dimer fatty acid and/or dimer fatty diol.

The invention further provides a polyurethane obtainable by reacting (i) a polyisocyanate, (ii) an unsaturated polyester polyol comprising at least 2 hydroxyl groups having a hydroxyl value of 11 to 225 mgKOH/g, which comprises the reaction product of at least one dicarboxylic acid and at least one polyol, wherein at least one of the acid and polyol comprises dimer fatty acid and/or dimer fatty diol, and optionally (iii) a chain extender.

The invention further provides the use of an unsaturated polyester polyol as defined herein as a building block in the formation of a polyurethane wherein the polyurethane is in the form of a foam, an elastomer, a coating, an adhesive, a dispersion for use in a coating or adhesive, or a thermoplastic material.

The invention further provides a polymer comprising (i) an olefinically unsaturated group, (ii) a group capable of reacting in the presence of water, and (iii) the reaction product of dimer fatty acid and/or dimer fatty diol.

The invention yet further provides a copolyester comprising a hard segment and a soft segment wherein the soft segment comprises an unsaturated polyester polyol as defined herein.

The invention still further provides a polyesteramide copolymer comprising at least one hard segment comprising at least one amide bond and at least one soft segment comprising an unsaturated polyester polyol as defined herein.

The unsaturated polyester polyol comprises the reaction product of an unsaturated dicarboxylic acid and/or polyol, which preferably comprises a single carbon double bond. An unsaturated dicarboxylic acid is preferred, suitably selected from at least one of the group consisting of maleic acid, fumaric acid, itaconic acid, ester and anhydride thereof; and preferably maleic acid, fumaric acid, and anhydride thereof. Particularly preferred is maleic anhydride.

The unsaturated polyester polyol according to the present invention comprises the reaction product of at least one dimer fatty acid and/or dimer fatty diol and/or equivalent thereof.

- 5 The term dimer fatty acid is well known in the art and refers to the dimerisation product of mono- or polyunsaturated fatty acids and/or esters thereof. Preferred dimer fatty acids are dimers of C₁₀ to C₃₀, more preferably C₁₂ to C₂₄, particularly C₁₄ to C₂₂, and especially C₁₈ alkyl chains. Suitable dimer fatty acids include the dimerisation products of oleic acid, linoleic acid, linolenic acid, palmitoleic acid, and
- 10 elaidic acid. The dimerisation products of the unsaturated fatty acid mixtures obtained in the hydrolysis of natural fats and oils, e.g. sunflower oil, soybean oil, olive oil, rapeseed oil, cottonseed oil and tall oil may also be used. Hydrogenated, for example by using a nickel catalyst, dimer fatty acids may also be employed.
- 15 In addition to the dimer fatty acids, dimerisation usually results in varying amounts of oligomeric fatty acids (so-called "trimer") and residues of monomeric fatty acids (so-called "monomer"), or esters thereof, being present. The amount of monomer can, for example, be reduced by distillation. Suitable dimer fatty acids have a dimer acid content of greater than 60%, preferably greater than 75%, more preferably in the range from 90 to 99.5%, particularly 92 to 99%, and especially 95 to 98% by
- 20 weight. The trimer content is suitably less than 40%, preferably in the range from 0.01 to 25%, more preferably 0.05 to 15%, particularly 0.1 to 5%, and especially 1 to 4% by weight. The monomer content is preferably less than 10%, more preferably in the range from 0.01 to 5%, particularly 0.01 to 1%, and especially 0.05 to 0.4% by weight. All of the above % by weight values are based on the total weight of trimer, dimer and monomer present.
- 25

- Dimer fatty diols can be produced by hydrogenation of the corresponding dimer fatty acid. Suitable dimer fatty diols have a dimer diol content of greater than 60%,
- 30 preferably greater than 75%, more preferably in the range from 90 to 99.5%, particularly 93 to 99%, and especially 94 to 98% by weight. The trimer content is suitably less than 40%, preferably in the range from 0.01 to 25%, more preferably 0.05 to 15%, particularly 0.1 to 5%, and especially 0.5 to 3% by weight. The monomer content is preferably less than 10%, more preferably in the range from 0.1 to 5%, particularly 0.3 to 4%, and especially 0.5 to 3% by weight. All of the above
- 35

% by weight values are based on the total weight of trimer, dimer and monomer present.

At least one polyol other than dimer fatty diol will be employed if there is no dimer fatty diol present in the unsaturated polyester polyol according to the present invention (i.e. dimer fatty acid is used). Other polyols may also be used in addition to dimer fatty diol.

The at least one other polyol suitably has a molecular weight of less than 400, preferably less than 300, more preferably less than 200, particularly in the range from 48 to 160, and especially 62 to 120. The at least one other polyol is preferably selected from the group consisting of pentaerythritol, glycerol, trimethylolpropane, ethylene glycol, diethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, dipropylene glycol, 1,4-butylene glycol, 1,6-hexylene glycol, neopentyl glycol, 3-methyl pentane glycol, 1,4-bis(hydroxymethyl) cyclohexane, 1,4-cyclohexane-dimethanol. Particularly preferred other polyols are diols such as ethylene glycol, diethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, dipropylene glycol, 1,4-butylene glycol, 1,6-hexylene glycol, neopentyl glycol, 3-methyl pentane glycol, 1,4-bis(hydroxymethyl)cyclohexane, 1,4-cyclohexane-dimethanol, and mixtures thereof; and particularly ethylene glycol, diethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, dipropylene glycol, 1,4-butylene glycol, 1,6-hexylene glycol and mixtures thereof.

Dicarboxylic acids other than dimer fatty acid and unsaturated dicarboxylic acids described herein can be used to produce the unsaturated polyester polyol according to the present invention. Aliphatic dicarboxylic acids are preferred, and suitable saturated acids are selected from the group consisting of adipic acid, glutaric acid, succinic acid, pimelic acid, suberic acid, azeleic acid, sebacic acid, heptane dicarboxylic acid, octane dicarboxylic acid, nonane dicarboxylic acid, decane dicarboxylic acid, undecane dicarboxylic acid, dodecane dicarboxylic acid and higher homologs thereof, and mixtures thereof. Particularly preferred other dicarboxylic acids include adipic acid, sebacic acid, azelaic acid, and mixtures thereof.

The unsaturated polyester polyol according to the present invention is preferably terminated at both ends with a hydroxyl group. Therefore the polyol is preferably present in molar excess to the dicarboxylic acids. The unsaturated polyester polyol is suitably formed from dicarboxylic acid to polyol, preferably diol, starting materials at a molar ratio in the range from 1:1.001 to 5.0, preferably 1:1.01 to 4.0, more preferably 1:1.2 to 3.0, particularly 1:1.4 to 2.0, and especially 1:1.5 to 1.7.

The unsaturated polyester polyol suitably has a number average molecular weight in the range from 500 to 10,000, preferably 600 to 8,000, more preferably 800 to 6,000, particularly 900 to 5,000, and especially 1,000 to 4,000.

The unsaturated polyester polyol preferably comprises on average less than 88, more preferably in the range from 1 to 45, particularly 2 to 25, and especially 3 to 15 ester bonds. In addition, the polyester preferably comprises on average (i) in the range from 1 to 15, more preferably 1 to 10, particularly 2 to 6, and especially 2 to 5 dimer residues, and/or (ii) less than 44, more preferably in the range from 1 to 26, particularly 2 to 20 and especially 3 to 10 carbon double bonds.

The unsaturated polyester polyol preferably has a hydroxyl value in the range from 14 to 190, more preferably 20 to 140, particularly 30 to 130, and especially 35 to 120 mgKOH/g. In addition, the polyester suitably has an acid value of less than 3.0, preferably less than 1.5, more preferably less than 1.3, and particularly less than 1.0 mgKOH/g, and/or a water content of less than 1%, more preferably less than 0.5%, particularly less than 0.2%, and especially less than 0.1%.

The unsaturated polyester polyol may be a liquid or a (semi-)crystalline solid, and is preferably liquid, at room temperature (25°C).

When the unsaturated polyester polyol is a liquid, the dynamic viscosity at 25°C is preferably in the range from 4,000 to 100,000, more preferably 6,000 to 80,000, particularly 8,000 to 70,000, and especially 10,000 to 65,000.

When the unsaturated polyester polyol is a solid, the melting point is preferably at least 40°C, more preferably in the range from 45 to 80°C, particularly 50 to 70°C, and especially 55 to 65°C.

A preferred unsaturated polyester polyol is derived from the reaction of an unsaturated dicarboxylic acid and dimer fatty diol. The dicarboxylic acid, suitably maleic anhydride, is preferably present in the range from 1 to 15%, more preferably 6.5 to 13%, and particularly 8 to 11% by weight; and the dimer fatty diol, for example Pripol™ 2033 (ex Uniqema), is preferably present from 85 to 99%, more preferably 87 to 93.5%, and particularly 89 to 92% by weight.

Another preferred unsaturated polyester polyol is derived from the reaction of an unsaturated dicarboxylic acid, dimer fatty acid and polyol. The dicarboxylic acid, suitably maleic anhydride, is preferably present in the range from 1 to 45%, more preferably 10 to 35%, and particularly 10 to 25% by weight; the dimer fatty acid, for example Pripol™ 1006 (ex Uniqema) is preferably present in the range from 5 to 85%, more preferably 10 to 75%, and particularly 30 to 65% by weight; and the polyol, suitably 1,3 propylene glycol, is preferably present in the range from 1 to 55%, more preferably 10 to 50%, and particularly 15 to 30% by weight.

A further preferred unsaturated polyester polyol is derived from the reaction of an unsaturated dicarboxylic acid, dimer fatty diol and polyol. The dicarboxylic acid, suitably maleic anhydride, is preferably present in the range from 1 to 45%, more preferably 10 to 40%, and particularly 20 to 30% by weight; the dimer fatty diol, example Pripol™ 2033 (ex Uniqema) is preferably present in the range from 5 to 85%, more preferably 10 to 75%, and particularly 25 to 60% by weight; and the polyol, suitably 1,3 propylene glycol, is preferably present in the range from 1 to 55%, more preferably 10 to 50%, and particularly 15 to 45% by weight.

The use of dicarboxylic acids and polyols other than unsaturated or dimer containing species enables properties such as OH value, molecular weight and level of unsaturation to be varied independently of each other.

For example an unsaturated polyester having a OH value 100 can be derived from (i) 7.2% maleic anhydride (MA), 21.4% propylene glycol (PG) and 71.4% dimer fatty acid (DFA) (preferably Pripol™ 1006); (ii) 11% MA, 23.5% PG and 65.5% DFA; (iii) 10.4% MA, 32.6% PG, 28.5% adipic acid and 28.5% DFA; (iv) 8% MA, 32% PG, 30% adipic acid and 30% DFA; (v) 46% MA, 27% PG and 27% dimer fatty diol (DFD) (preferably Pripol™ 2033); and (vi) 46% MA, 38% PG and 16% DFD.

Also an unsaturated polyester having an OH value 35 can be derived from (i) 7.5% MA, 17.9% PG and 74.6% DFA; (ii) 11.6% MA, 20.4% PG and 68% DFA; (iii) 8.6% MA, 29.1% PG, 31.1% adipic acid and 31.2% DFA; (iv) 10.9% MA, 29.9% PG, 29.6% adipic acid and 29.6% DFA; (v) 26% MA, 19% PG and 55% DFD; and (vi) 48% MA, 37% PG and 15% DFD.

The polyurethane according to the present invention is obtainable by reacting a polyisocyanate, an unsaturated polyester polyol as defined herein, and optionally a chain extender. The polyurethane may for example be a coating or dispersion for a coating or adhesive, an elastomer, a thermoplastic e.g. a rubber or adhesive, or a foam.

The polyisocyanate is preferably at least one isocyanate which has a functionality of at least 2, and may be an aliphatic isocyanate such as hexamethylene 1,6-diisocyanate, but more preferably is an aromatic isocyanate such as tolylene diisocyanate (TDI), m-phenylene diisocyanate, p-phenylene diisocyanate, xylylene diisocyanate, 4,4'-diphenylmethane diisocyanate (MDI), hexamethylene diisocyanate, isophorone diisocyanate (IPDI), polymethylenepolyphenyl diisocyanate, 3,3'-dimethyl-4,4'-biphenylene diisocyanate, 3,3'-dimethyl-4,4'-diphenylmethane diisocyanate, 3,3'-dichloro-4,4'-biphenylene diisocyanate, 1,5-naphthalene diisocyanate, or modified compounds thereof such as uretonimine-modified compounds thereof. The polyisocyanate monomers can be used alone or as mixtures thereof. In a preferred embodiment, (modified) 4,4'-diphenylmethane diisocyanate (MDI), tolylene diisocyanate (TDI) and/or isophorone diisocyanate (IPDI) is/are used.

In one embodiment of the invention, at least one of the aforementioned polyisocyanates is reacted with at least one of the aforementioned unsaturated polyester polyols to form a prepolymer. The molar ratio of polyisocyanate to unsaturated polyester starting materials which are mixed together to react to form the prepolymer is preferably in the range from 20 to 80%:20 to 80%, more preferably 35 to 75%:25 to 65%, particularly 45 to 70%:30 to 55%, and especially 55 to 70%:30 to 45%. The polyisocyanate is preferably used in molar excess relative to OH group content of the polyester, so as to obtain a reaction mixture containing isocyanate-terminated prepolymer and sufficient unreacted

polyisocyanate, such that the later addition of any chain extender can result in reaction to form the polyurethane, without the requirement for adding further polyisocyanate.

- 5 The prepolymer reaction mixture preferably has an isocyanate content in the range from 0 to 15%, more preferably 0.1 to 8%, particularly 0.5 to 4%, and especially 1.5 to 3.5% NCO.

- 10 Other monomers, such as acrylic acid or acrylates may be incorporated into the polyurethane prepolymer, and/or the prepolymer may be blended with other polymers, such as acrylates.

The prepolymer may be used for example to make polyurethane dispersions, thermoplastic polyurethanes, and polyurethane foams.

- 15 For use in making polyurethane dispersions, the prepolymer may be chain extended, either prior to or after dispersing in water. If no chain extender is used, the unsaturated polyester polyol may be used in molar excess to the isocyanate, so as to obtain a hydroxyl terminated polymer, giving a non-reactive polyurethane. The prepolymer reaction mixture preferably has an isocyanate content in the range from 0 to 6%, more preferably 0.2 to 5%, particularly 0.5 to 4%, and especially 2 to 3.5% NCO. For a non-reactive polyurethane dispersion the isocyanate content is preferably 0%.

- 25 The polyurethane dispersion described herein may be blended with other polymer dispersions, for example poly-vinylacetate, poly-vinylacetate-ethylene or poly-acrylate dispersions.

- 30 For thermoplastic polyurethanes, the molar ratio of polyisocyanate to unsaturated polyester polyol starting materials which are mixed together to react to form the prepolymer is preferably in the range from 20 to 80%:20 to 80%, more preferably 25 to 65%:35 to 75%, particularly 30 to 55%:45 to 70%, and especially 30 to 50%:50 to 70%.

The prepolymer can be chain extended. Starting materials for thermoplastic polyurethanes can be reacted in the mould of the final product. In that case, the optional chain extender is reacted into the polyurethane. The polyester is preferably used in molar excess or nearly equimolar amount relative to NCO content of the polyisocyanate, leaving little or no isocyanate reactive groups for moisture curing.

For polyurethane foams, water is normally included in the reaction mixture to promote gas bubble formation, caused by reaction of water with isocyanate which forms carbon dioxide gas. For flexible foams, typically 2 to 3% water is used. For rigid foams, less water is used, but other blowing agents can be added. The molar ratio of polyisocyanate to unsaturated polyester polyol starting materials which are mixed together to react to form the prepolymer is preferably in the range from 20 to 80%:20 to 80%, more preferably 25 to 65%:35 to 75%, particularly 25 to 55%:45 to 75%, and especially 30 to 45%:55 to 70%. The ratio of polyisocyanate to polyester is adjusted so that the water in the formulation reacts with polyisocyanate, leaving enough isocyanate reactive groups to react with the polyester. The polyester is preferably used in molar excess or nearly equimolar amount relative to NCO content of the polyisocyanate after subtracting the NCO amount reacting with water in the formulation, leaving little or no isocyanate reactive groups for moisture curing.

The chain extender component which may be used to form the polyurethane according to the present invention suitably comprises a low molecular compound having 2 or more active hydrogen groups, for example polyols such as ethylene glycol, diethylene glycol, propylene glycol, 1,4-butylene glycol, 1,5-pentylene glycol, methylpentanediol, 1,6-hexylene glycol, neopentyl glycol, trimethylolpropane, hydroquinone ether alkoxylate, resorcinol ether alkoxylate, glycerol, pentaerythritol, diglycerol, dextrose, and a 1,4:3,6 dianhydrohexitol such as isomannide, isosorbide and isoidide; aliphatic polyhydric amines such as ethylenediamine, hexamethylenediamine, and isophorone diamine; aromatic polyhydric amines such as methylene-bis(2-chloroaniline), methylenebis(dipropylaniline), diethyl-toluenediamine, trimethylene glycol di-p-aminobenzoate; alkanolamines such as diethanolamine, triethanolamine and diisopropanolamine; and polyoxyalkyleneamines.

In one embodiment of the invention, the unsaturated polyester polyol may be added together with the chain extender to react in order to form the polyurethane. The unsaturated polyester polyol employed may be the same as or different to the unsaturated polyester polyol used to form the prepolymer.

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The amount of chain extender to unsaturated polyester polyol employed is preferably in the range from 0 to 80% by weight, more preferably 0 to 50%, particularly 0 to 30%, and especially 0 to 15% by weight, the amount depending on the properties required for each application.

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The use of the unsaturated polyester polyol described herein means that there are dual curing sites to provide enhanced properties of polyurethanes according to the present invention. For example polyurethane coatings can have improved hardness, durability and scratch resistance, heat and solvent resistance, and/or good processability. Polyurethane elastomers can have improved heat and solvent resistance.

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The unsaturated polyester polyol according to the present invention may also be used as a building block for formation of polymers, other than polyurethanes, which also contain groups capable of reacting in the presence of moisture, for example alkoxy silane groups. The unsaturated polyester polyol may for example be reacted with an alkoxy silane to form polyhydroxysilane polymers having dual curing sites, i.e. both moisture curable and UV curable sites. In one embodiment, polymers formed from the unsaturated polyester polyol may comprise both alkoxy silane and urethane groups.

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The unsaturated polyester polyol may also be used as a building block for the formation of other polymers such as polyester copolymers and polyesteramide copolymers.

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Thus, a further embodiment of the present invention is a copolyester, preferably a block copolymer, comprising a hard segment and a soft segment wherein the soft segment comprises an unsaturated polyester polyol as defined herein.

The composition of the copolyester hard segment may vary over a wide range. The hard segment is preferably an aromatic polyester. Suitable aromatic dicarboxylic acids, and/or ester derivatives thereof, for use in forming the hard segment, include terephthalic acid, isophthalic acid, naphthalene dicarboxylic acid, diphenyl
5 dicarboxylic acid, or mixtures thereof. Terephthalic acid, and/or ester derivative thereof, is particularly preferred. The hard segment is preferably formed from greater than 50, more preferably greater than 70, particularly greater than 90, and especially greater than 95 and up to 100 mole % of aromatic dicarboxylic acid(s) and/or ester derivatives thereof. The balance (up to 100 mole %) of dicarboxylic
10 acids (if any) can be suitably made up of aliphatic dicarboxylic acids, such as adipic acid, sebacic acid, or cyclohexane dicarboxylic acid.

Suitable diols or glycols for use in forming the hard segment include aliphatic diols such as ethylene glycol, 1,3-propylene glycol, 1,4-butanediol, 1,6-hexanediol,
15 neopentyl glycol, trimethylene glycol, tetramethylene glycol, and cyclohexane dimethanol, or aromatic diols such as 2,2-bis(4-hydroxyphenyl)propane. The hard segment is preferably formed from greater than 50, more preferably greater than 70, particularly greater than 90, and especially greater than 95 and up to 100 mole % of aliphatic glycol(s), preferably ethylene glycol and/or 1,4-butanediol.

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In a particularly preferred embodiment, the hard segment is polybutylene terephthalate, polyethylene terephthalate, polyethylene naphthalate or mixtures thereof, and especially polybutylene terephthalate.

25 The hard segment preferably has a molecular weight number average in the range from 1,000 to 30,000, more preferably 2,000 to 15,000, particularly 2,500 to 10,000, and especially 3,000 to 5,000.

The hard segment preferably has a melting point (T_m) in the range from 200 to
30 280°C, more preferably 210 to 270°C, particularly 215 to 255°C, and especially 220 to 230°C.

The ratio of hard to soft segment present in the copolyester is preferably in the range from 1 to 20:1, more preferably 2 to 15:1, particularly 3 to 10:1, and
35 especially 4 to 6:1 by weight %.

The copolyester preferably has a molecular weight number average in the range from 5,000 to 100,000, more preferably 15,000 to 80,000, particularly 25,000 to 60,000, and especially 30,000 to 40,000.

- 5 The copolyester preferably has a melting point (T_m) in the range from 200 to 280°C, more preferably 210 to 265°C, particularly 215 to 245°C, and especially 220 to 225°C; and/or a glass transition temperature (T_g) in the range from -80 to -40°C, more preferably -70 to -45°C, particularly -65 to -50°C, and especially -60 to -55°C.
- 10 The copolyester described herein may be used in a wide range of applications where thermoplastic elastomers are normally used, such as bearings and seals, belts, boots and bellows, coiled tubing, reinforced housing, electric cables, electric switches for appliances, and all types of automotive parts.
- 15 A further embodiment of the invention is a copolyesteramide, preferably a block copolymer, comprising at least one hard segment comprising at least one amide bond and at least one soft segment comprising an unsaturated polyester polyol as defined herein.
- 20 The hard segment of the copolyesteramide according to the present invention comprises at least one, preferably in the range from 2 to 35, more preferably 3 to 20, particularly 4 to 15, and especially 5 to 10 amide bonds. Thus, the hard segment is preferably an oligoamide or polyamide (hereinafter referred to as polyamide).
- 25 The composition of the hard segment may vary over a wide range. Polyamide is normally produced in a condensation reaction between a dicarboxylic acid and a diamine.
- 30 There are two major classes of dicarboxylic acids which are normally used to form polyamides, namely dimer fatty acids and non-dimer fatty acids.
- 35 Suitable dimer fatty acids are described herein. Suitable non-dimer fatty acids may be aliphatic or aromatic, and include dicarboxylic acids and the esters, preferably alkyl esters, thereof, preferably linear dicarboxylic acids having terminal carboxyl

groups having a carbon chain of from 2 to 20, more preferably 6 to 12 carbon atoms, such as adipic acid, pimelic acid, suberic acid, azeleic acid, sebacic acid, heptane dicarboxylic acid, octane dicarboxylic acid, nonane dicarboxylic acid, decane dicarboxylic acid, undecane dicarboxylic acid, dodecane dicarboxylic acid and higher homologs thereof.

The polyamide hard segment is preferably formed from dimer fatty acids to non-dimer fatty acids present at a ratio of from 0 to 100%:0 to 100%, more preferably 50 to 100%:0 to 50%, and particularly 80 to 100%:0 to 20% by weight of the total dicarboxylic acids.

Suitable diamines include amine-equivalents of the aforementioned dicarboxylic acids, but generally shorter chain materials are preferred, particularly those containing from 2 to 7 carbon atoms. Diamines such as ethylenediamine, propylenediamine, tetramethylenediamine, pentamethylenediamine, hexamethylenediamine, as well as dimer fatty diamines (derived from dimer fatty acids) are preferred. Suitable aromatic diamines include materials derived from benzene, toluene and other substituted aromatic materials, such as 2, 6-tolylenediamine, 4, 4-diphenylmethanediamine and xylylenediamine. Other suitable diamines include those which contain one or two secondary amino groups, and heterocyclic diamines, for example piperazine. Branched diamines, such as 3-methyl pentane diamine may also be used.

The polyamide may also be unsaturated. For example the polyamide may be formed from an unsaturated dicarboxylic acid, preferably selected from at least one of the group consisting of maleic acid, fumaric acid, itaconic acid, ester and anhydride thereof; and preferably maleic acid, fumaric acid, and anhydride thereof. Particularly preferred is maleic anhydride.

The unsaturated polyamide preferably comprises dimer fatty acid and/or dimer fatty diamine. Unsaturated polyamide can be produced which may be seen as equivalent to the unsaturated polyester polyol described herein, wherein polyamine, preferably diamine, is used instead of polyol. The dimer containing unsaturated polyamide may be produced separately prior to reaction with the unsaturated polyester polyol to form the copolyesteramide. The dimer containing unsaturated

polyamide may also have separate utility by forming polymers by reacting with other materials, for example polyisocyanate as described herein, to form polyurea which also has both moisture curable and UV curable sites.

5 The ratio of dicarboxylic acid to diamine starting materials used to form the polyamide segment is preferably in the range from 1.0 to 5.0:1, more preferably 1.05 to 3.0:1, particularly 1.1 to 2.0:1, and especially 1.2 to 1.4:1. The polyamide is preferably carboxy terminated at both ends, particularly by dimer fatty acids as described herein.

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The hard segment is suitably a block, preferably having a molecular weight number average in the range from 500 to 15,000, more preferably 1,000 to 10,000, particularly 1,500 to 6,000, and especially 2,000 to 4,000.

15 The hard segment preferably has a softening point in the range from 60 to 200°C, more preferably 65 to 150°C, particularly 70 to 125°C, and especially 75 to 100°C.

The ratio of hard segment to soft segment present in the copolyesteramide is preferably in the range from 1 to 25:1, more preferably 4 to 20:1, particularly 6 to 20 15:1, and especially 8 to 10:1 by weight.

The copolyesteramide preferably has a molecular weight number average in the range from 5,000 to 80,000, more preferably 10,000 to 50,000, particularly 13,000 to 30,000, and especially 15,000 to 20,000.

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The copolyesteramide preferably has a softening point in the range from 60 to 200°C, more preferably 65 to 150°C, particularly 70 to 125°C, and especially 75 to 100°C; and/or a glass transition temperature (T_g) in the range from -60 to 0°C, more preferably -50 to -10°C, particularly -40 to -20°C, and especially -35 to -25°C.

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The invention is illustrated by the following non-limiting examples.

In this specification, the following test methods have been used.

(i) Molecular weight (number average) was determined by Gel Permeation
35 Chromatography.

- (ii) OH value is defined as the number of mg of potassium hydroxide equivalent to the hydroxyl content of 1 g of sample, and was measured by acetylation followed by hydrolysis of excess acetic anhydride. The acetic acid formed was subsequently titrated with an ethanolic potassium hydroxide solution.
- 5 (iii) Acid value is defined as the number of mg of potassium hydroxide required to neutralise the free fatty acids in 1 g of sample, and was measured by direct titration with a standard potassium hydroxide solution.
- (iv) The isocyanate (NCO) value is defined as the weight % content of isocyanate in the sample and was determined by reacting with excess dibutylamine, and back
- 10 titrating with hydrochloric acid.
- (v) Dynamic viscosity was measured at 25°C using a Brookfield Rheometer.
- (vi) Water content was analysed by titration according to the Karl-Fischer method.
- (vii) The glass transition temperature (T_g) was measured by Differential Scanning Calorimetry (DSC) at a scan rate of 20°C/minute using a Mettler DSC30.
- 15 (viii) The feel or touch of a polyurethane dispersion applied to a textile was determined by a test panel and rated on a scale of 1 to 5, with 1 being soft, 3 being medium soft, and 5 being hard.
- (ix) The adhesion of a polyurethane dispersion applied to rubber was determined according to DIN 53151. The adhesion was rated on a scale of 0 to 5, with 0 being
- 20 0% adhesion loss, and 5 being > 65% adhesion loss.

Examples

Example 1

- 25 2310.2 g dimer fatty diol (PripolTM 2033 (ex Uniqema) and 300 g maleic anhydride (ex Merck) were added to a glass reactor and the temperature was gradually increased to 225°C. Water was removed via distillation during the heating process. After about one hour, the reaction was catalysed with 0.005 wt% of a 20 wt% titanium tetrabutoxide (TBT) solution (ex Merck). The reaction was continued at
- 30 225°C until the acid value was <1.0 mg KOH/g. The unsaturated polyester polyol product exhibited the following properties:

	Molecular weight (number average)	1983
	Acid value	0.57 mgKOH/g
35	OH value	56 mgKOH/g

Water content	0.01%
Dynamic viscosity at 25°C	27,800 mPa.s

Example 2

5 2426.1 g dimer fatty diol (Pripol™ 2033) and 186.6 g maleic anhydride (ex Merck) were reacted together at 225°C according to the procedure of Example 1, except there was no catalyst present. The unsaturated polyester polyol product exhibited the following properties:

10 Molecular weight (number average)	974
Acid value	1.19 mgKOH/g
OH value	114 mgKOH/g
Water content	0.01%
Dynamic viscosity at 25°C	6850 mPa.s

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Example 3

1718.2 g dimer fatty acid (Pripol™ 1009, ex Uniqema) 235 g maleic anhydride (ex Merck) and 625.9 g propylene glycol (ex Merck) were reacted at 225°C according to the method of Example 1. After approximately one hour at 225°C, 0.13 ml of 20 wt% TBT was added to the reaction mixture. After about a further 5 hours, when the acid value was about 0.4, the pressure was gradually reduced to 1 mbar to distil off the excess propylene glycol. The distillation was stopped when 105.7 g propylene glycol and the unsaturated polyester polyol product had been distilled off. The unsaturated polyester polyol was cooled (under full vacuum) to 150°C and then filtered. The unsaturated polyester polyol product exhibited the following properties:

25 Molecular weight (number average)	1900
Acid value	0.28 mgKOH/g
OH value	59 mgKOH/g
30 Water content	0.01%
Dynamic viscosity at 25°C	343,000 mPa.s

Example 4

2504.8 g dimer fatty diol (Pripol™ 2033) and 368.2 g maleic anhydride (ex Merck) were reacted at 225°C according to the procedure of Example 1 with catalysis with

35

0.005 wt% of 20 wt% TBT solution. The unsaturated polyester polyol product exhibited the following properties:

	Molecular weight (number average)	2820
5	Acid value	0.8 mgKOH/g
	OH value	39 mgKOH/g
	Water content	0.01 %
	Dynamic viscosity at 25°C	63,500 mPa.s

10 **Example 5**

A polyurethane was produced according to the following composition:

		<u>Parts by weight</u>
	Polyester polyol prepared in Example 3	142
15	N-methylpyrrolidone (NMP)	35
	Dimethylol propionic acid (DMPA)	13.5
	Isophorone diisocyanate (IPDI)	55
	Dibutyl tin dilaurate (DBTL)	0.2
	Triethylene amine (TEA)	9.6
20	Jeffamine D230	13.4
	Water	350

The unsaturated polyester polyol and 85% of the NMP were charged into a reactor equipped with a partial condensor, total condensor, agitator inert gas sparge and thermometer. The mixture was heated to 80-100°C, and when the mixture was homogeneous, the DMPA was added and vacuum applied until the mixture became homogeneous again (approx. 15 mins.). The mixture was cooled to 65°C, the DBTL added, and the IPDI was dosed over a period of one hour. After addition was complete, the temperature was raised to 70-75°C. The reaction was continued until a constant NCO value was obtained (approx. 2.5%). The temperature was reduced to 65°C and the TEA and the remaining 15% NMP added over a 10 minutes period. Stirring was continued for 15 minutes. The resultant prepolymer was added to the water at 25°C, and stirred for 30 minutes at this temperature. The Jeffamine D230 was added (in water) over a period of 15 minutes, keeping the temperature below 30°C and stirring was continued for 2 hours. The resultant polyurethane dispersion

resin product had a pH around 8 and contained approximately 35 wt% non volatiles, 4.5 wt% volatiles.

Example 6

5 This is a comparative example not according to the present invention.

A polyurethane dispersion was produced according to Example 5 except that a saturated dimer fatty acid based polyester polyol was used instead of the unsaturated polyester polyol. The saturated polyester polyol had a molecular
10 weight of 2000 g/mol, and was formed from and a 50/50 weight ratio of adipic acid and dimer fatty acid (Pripol™ 1006, ex Uniqema), and 1,6-hexanediol.

Example 7

The polyurethane dispersions produced in Examples 5 and 6 were tested for feel on
15 textile, and adhesion to rubber according to the test procedures described herein. The results are shown in Table 1.

Table 1

<u>Example No</u>	<u>Textile Feel</u>	<u>Adhesion to Rubber</u>
5	2	1-2
6 (Comparative)	5	5

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The polyurethane dispersion according to the present invention exhibited softer feel on textile, and improved adhesion on rubber.

The above examples illustrate the improved properties of an unsaturated polyester
25 polyol and polyurethane according to the present invention.

Claims

1. An unsaturated polyester polyol comprising at least 2 hydroxyl groups has a hydroxyl value of 11 to 225 mgKOH/g and comprises the reaction product of at least one dicarboxylic acid and at least one polyol, wherein at least one of the acid and polyol comprises dimer fatty acid and/or dimer fatty diol.
5
2. An unsaturated polyester polyol according to claim 1 which is terminated at both ends with a hydroxyl group.
- 10 3. An unsaturated polyester polyol according to either one of claims 1 and 2 which is formed from dicarboxylic acid to polyol starting materials at a molar ratio in the range from 1:1.001 to 5.0.
4. An unsaturated polyester polyol according to any one of the preceding claims wherein the number average molecular weight is 500 to 10,000.
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5. An unsaturated polyester polyol according to any one of the preceding claims comprising the reaction product of dimer fatty diol.
- 20 6. An unsaturated polyester polyol according to any one of the preceding claims comprising the reaction product of a polyol having a molecular weight of less than 400.
7. An unsaturated polyester polyol according to any one of the preceding claims comprising on average (i) 1 to 45 ester bonds, (ii) 1 to 10 dimer residues, and/or (iii) 1 to 26 carbon double bonds.
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8. An unsaturated polyester polyol according to any one of the preceding claims having an acid value of less than 1.5 mgKOH/g.
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9. An unsaturated polyester polyol according to any one of the preceding claims which is obtainable by reacting (i) an unsaturated dicarboxylic acid and dimer fatty diol, (ii) an unsaturated dicarboxylic acid, dimer fatty acid and polyol, or (iii) an unsaturated dicarboxylic acid, dimer fatty diol and polyol.
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10. An unsaturated polyester polyol according to claim 9 wherein the weight ratio of (i) unsaturated dicarboxylic acid to dimer fatty diol is 6.5 to 13%:87 to 93.5%, (ii) unsaturated dicarboxylic acid to dimer fatty acid to polyol is 10 to 35%:10 to 75%:10 to 50%, or (iii) unsaturated dicarboxylic acid to dimer fatty diol to polyol is 10 to 40%:10 to 75%:10 to 50%.
11. A process for preparing an unsaturated polyester polyol having a hydroxyl value of 11 to 225 mgKOH/g which comprises reacting at least one dicarboxylic acid and at least one polyol at a molar ratio in the range from 1:1.01 to 5.0, wherein at least one of the acid and polyol comprises dimer fatty acid and/or dimer fatty diol.
12. A polyurethane obtainable by reacting (i) a polyisocyanate, (ii) an unsaturated polyester polyol comprising at least 2 hydroxyl groups having a hydroxyl value of 11 to 225 mgKOH/g, which comprises the reaction product of at least one dicarboxylic acid and at least one polyol, wherein at least one of the acid and polyol comprises dimer fatty acid and/or dimer fatty diol, and optionally (iii) a chain extender.
13. A polyurethane according to claim 12 in the form of a prepolymer wherein the molar ratio of polyisocyanate to unsaturated polyester starting materials is 35 to 75%:25 to 65%.
14. A polyurethane according to claim 13 wherein the prepolymer reaction mixture has an isocyanate content of 0.1 to 8% NCO.
15. Use of an unsaturated polyester polyol comprising at least 2 hydroxyl groups having a hydroxyl value of 11 to 225 mgKOH/g which comprises the reaction product of at least one dicarboxylic acid and at least one polyol, wherein at least one of the acid and polyol comprises dimer fatty acid and/or dimer fatty diol, as a building block in the formation of a polyurethane wherein the polyurethane is in the form of a foam, an elastomer, a coating, an adhesive, a dispersion for use in a coating or adhesive, or a thermoplastic material.
16. A polymer comprising (i) an olefinically unsaturated group, (ii) a group capable of reacting in the presence of water, and (iii) the reaction product of dimer fatty acid and/or dimer fatty diol.

17. A polymer according to claim 16 wherein the group capable of reacting in the presence of water is an isocyanate and/or an alkoxysilane group.

5 18. A polymer according to either one of claims 16 and 17 which is formed from (i) an unsaturated polyester polyol comprising at least 2 hydroxyl groups having a hydroxyl value of 11 to 225 mgKOH/g, which comprises the reaction product of at least one dicarboxylic acid and at least one polyol, wherein at least one of the acid and polyol comprises dimer fatty acid and/or dimer fatty diol, and/or (ii) an
10 unsaturated polyamide comprising at least 2 amine groups which comprises the reaction product of at least one dicarboxylic acid and at least one polyamine, wherein at least one of the acid and polyamine comprises dimer fatty acid and/or dimer fatty diamine.

15 19. A polymer according to claim 18 wherein the unsaturated polyester polyol and/or the unsaturated polyamide are reacted with an isocyanate and/or an alkoxysilane group.

20 20. A copolyester comprising a hard segment and a soft segment wherein the soft segment comprises an unsaturated polyester polyol as defined herein.

21. A polyesteramide copolymer comprising at least one hard segment comprising at least one amide bond and at least one soft segment comprising an unsaturated polyester polyol as defined herein.

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