POLYURETHANE BASED SYNTHETIC LEATHERS COMPRISING NANO PARTICLES AND HAVING IMPROVED PEEL STRENGTH

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Appl. No.: 14/431,533

PCT Filed: Oct. 16, 2012

PCT No.: PCT/CN2012/083026

§ 371 (c)(1), (2) Date: Mar. 26, 2015

Abstract

Disclosed herein are methods of producing externally stabilized, poromeric synthetic leathers having improved peel strength, the methods comprising: preparing a prepolymer from a mixture comprising at least one polyester polyol, at least one polyether polyol, at least one isocyanate and optionally in a solvent; mixing the prepolymer, water, and a first surfactant; optionally add a second chain extender to form a PUD; preparing a mixture comprising said PUD, at least one surfactant, and at least one thickener; frothing said mixture; applying the frothed mixture to a fabric and thereby forming a coated fabric; adjusting the thickness of the frothed mixture on the coated fabric; drying the coated fabric. Methods of improving the peel strength of poromeric synthetic leathers are also disclosed. Externally stabilized synthetic leathers having improved peel strength are also disclosed.
POLYURETHANE BASED SYNTHETIC LEATHERS COMPRISING NANO-PARTICLES AND HAVING IMPROVED PEEL STRENGTH

BACKGROUND OF THE INVENTION

[0001] Currently, most polyurethane (PU) synthetic leathers are made using organic solvents, such as dimethyl formamide, methyl ethyl ketone (MEK) and toluene. These solvents vaporize during manufacture and post manufacturing, which leads to potential health issues for the manufacturing staff, the end users of the synthetic leather, and the environment. As a result, the European standard for the solvent PU based synthetic leather was changed to require less than 10 ppm DMF in the leather. Making such leathers is a challenge using organic solvent based methodologies. As a result, the use of solvent free or water borne PU (also known as polyurethane dispersion or PUD) has received attention, as it uses little, if any, organic solvent.

[0002] PUD is an aqueous emulsion of PU particles in water having high solid content, small particle size, and prolonged stability (up to six months or longer). When making synthetic leather using PUD the following general method is used: 1) PUD is frothed 2) the frothed PUD is applied to a fabric, 3) the thickness of the frothed PUD is adjusted using methods known in the art, and 4) the now coated fabric is cured to form a synthetic leather having a poromeric layer. See U.S. Pat. No. 7,306,825 for an example of this methodology.

[0003] Synthetic leather derived from PUD is similar to that made from PU and an organic solvent. It is breathable, and has good hand feel. More importantly, the PUD synthetic leather is low in volatile organic compounds. Typically, the PUD in the PUD based synthetic leather is made by combining a diisocyanate and a polyol. The resulting product is then dispersed in water to make the PUD. While such synthetic leathers have high solid content and nice hand feel, they have poor peel strength. Thus, it would be advantageous to develop a PUD based synthetic leather that had improved peel strength performance.

SUMMARY OF THE INVENTION

[0004] In one aspect, disclosed herein are methods for producing externally stabilized, poromeric synthetic leathers having improved peel strength, the methods comprising:

[0005] preparing a prepolymer from a mixture comprising at least one polyester polyol, at least one polyester polyol, at least one isocyanate and optionally in a solvent;

[0006] mixing the prepolymer, water, and a first surfactant;

[0007] optionally add a second chain extender to form a PUD;

[0008] preparing a mixture comprising said PUD, at least one surfactant, and at least one thickener;

[0009] frothing said mixture;

[0010] applying the frothed mixture to a fabric and thereby forming a coated fabric;

[0011] adjusting the thickness of the frothed mixture on the coated fabric;

[0012] drying the coated fabric.

[0013] In another aspect, disclosed herein are methods of improving the peel strength of poromeric synthetic leathers, the methods comprising:

[0014] preparing a prepolymer from a mixture comprising at least one polyester polyol, at least one polyester polyol, at least one isocyanate and optionally in a solvent;

[0015] mixing the prepolymer, water, and a first surfactant;

[0016] optionally add a second chain extender to form a PUD;

[0017] preparing a mixture comprising said PUD, at least one surfactant, and at least one thickener;

[0018] frothing said mixture;

[0019] applying the frothed mixture to a fabric and thereby forming a coated fabric;

[0020] adjusting the thickness of the frothed mixture on the coated fabric;


[0022] In another aspect, poromeric, synthetic leathers having improved peel strength made according to the aforementioned methods are also disclosed herein.

[0023] The PUD based synthetic leathers disclosed herein are externally stabilized, i.e., they require the presence of at least one surfactant that does not react with the PUD. Likewise, the methods disclosed herein utilize externally stabilized PUDs.

[0024] The PUD based synthetic leathers disclosed herein may be used to make synthetic leather for any leather or synthetic leather applications. Particular examples include footwear, handbags, belts, purses, garments, furniture upholstery, automotive upholstery, and gloves.

DESCRIPTION OF THE FIGURES

[0025] FIG. 1 is a picture of the cross section of a polyester polyol free synthetic leather, where the coated fabric has long fibers (Control 1).

[0026] FIG. 2 is a picture of the cross section of a polyester polyol free synthetic leather, where the coated fabric has short fibers (Control 2).

[0027] FIG. 3 is a picture of the cross section of a polyester polyol containing synthetic leather, where the coated fabric has long fibers (Example 1).

[0028] FIG. 4 is a picture of the cross section of a polyester polyol containing synthetic leather, where the coated fabric has short fibers (Example 2).

DETAILED DESCRIPTION

[0029] The methods and leathers disclosed herein require the incorporation of at least one polyester polyol, at least one polyester polyol and at least one isocyanate into the PUD.

[0030] Polyester polyols, are compounds that have an ester containing backbone and further comprise at least two OH groups. They are typically made from aliphatic organic dicarboxylic acids with 2 to 12 carbons, preferably aliphatic dicarboxylic acids with 4 to 6 carbons, and multivalent alcohols, preferably diols, with 2 to 12 carbons. Examples of aliphatic dicarboxylic acids include succinic acid, glutaric acid, adipic acid, suberic acid, azelaic acid, sebacic acid, decanedioic acid, maleic acid, fumaric acid, phthalic acid, isophthalic acid, and terephthalic acid. The corresponding dicarboxylic acid derivatives may also be used such as dicarboxylic acid mono- or di-esters of alcohols with 1 to 4 carbons, or dicarboxylic acid anhydrides. Examples of divalent and multivalent alcohols, especially diols, include ethanediol, diethylene glycol, glycerine and trimethylolpro-
Polymer polyols are compounds that have an ether backbone and further comprise at least two OH groups. Polymer polyols are commonly made by reacting monomeric compounds (either alone or in combination), such as glycercine (a triol), pentaerythritol (a tetrol), ethylene glycol (a diol), diethylene glycol (a diol of the formula: HO(\(\text{CH}_2\text{CH}_2\text{O}\))\(\text{CH}_2\text{CH}_2\text{OH}\)), and/or sucrose with ethylene oxide, propylene oxide and/or butylene oxide in the presence of an initiator and/or a catalyst. Suitable initiators include aliphatic and aromatic amines, such as monoethanolamine, vicinal tolenediamines, ethylenediamines, and propylenediamine. Useful catalysts include strong bases, such as NaOH, or KOH, and double metal cyanide catalysts, such as zinc hexacyanocobalt-t-butanol complex. Common polymer polyols include polyethylene glycol (PEG), polypropylene glycol, and poly(tetramethylethylene ether)glycol.

The use of a strong base catalyst to make a polyester polyol often causes the polyester polyol to be too basic, which has a detrimental effect on the aforementioned prepolymer. Consequently, it is often necessary to treat the polyester polyol with a scavenger compound, which reacts with the residual base and makes the prepolymer more acidic. Suitable scavenger compounds include benzoyl chloride, and 85% phosphoric acid, with benzoyl chloride being preferred. Typically, adding aqueous acids introduces excess water into the prepolymer, which will react with the isocyanate and adversely impact the resulting leather. The inventors typically use a scavenger compound to adjust the net controlled polymerization rate of the mixture to be lower than ~10. ASTM D 6437-05 corresponds to the CPR procedure.

The isocyanates used herein contain at least two isocyanate groups and include organic disiocyanates, which may be aromatic, aliphatic, or cycloaliphatic, or a combination thereof. Representative examples of suitable disiocyanates include 4,4'-disiocyanatodiphenylmethane, 2,4'-disiocyanatodiphenylmethane, isophorone disiocyanate, p-phenylene disiocyanate, 2,6 toluene disiocyanate, polyphenyl polyisocyanate, 1,3-bis(isocyanatophenylethyl)cylohexane, 1,4-diisocyanatocylohexane, hexamethylene disiocyanate, 1,5-naphthalene disiocyanate, 3,3'-dimethyl-4,4'-biphenyl disiocyanate, 4,4'-diisocyanatocyclohexylmethane, 2,4'-diisocyanatodicyclohexylmethane, and 2,4-toluene disiocyanate, or combinations thereof. More preferred disiocyanates are 4,4'-diisocyanatodicyclohexylmethane, 4,4'-diisocyanatodialkylphenylmethane, 2,4'-diisocyanatodicyclohexylmethane, and 2,4'-diisocyanatodiphenylmethane. Most preferred are isophorone disiocyanate; 4,4'-diisocyanatodiphenylmethane (also known as 4,4'-MDI); and 2,4'-diisocyanatodiphenylmethane (also known as 2,4'-MDI). The isocyanates may be purified or part of a mixture of one or more isocyanates. If an isocyanate is a solid, it may be melted and/or dissolved in a solvent before it is reacted with the at least one polyester polyol and the at least one polyester polyol.

The PUDs disclosed herein are made by reacting at least one polyester polyol at least one polyester polyol and at least one isocyanate, optionally in a solvent (wherein the solvent does not or minimally reacts with the isocyanate). This affords a prepolymer, which is then added to a mixture comprising a solvent that is comprised of water, at least one surfactant, and at least one chain extender. The mixture may be stirred or mixed using methods known in the art. The resulting polyurethane dispersion (PUD) has a “milky-like” appearance. The polyester polyol to the polyether ratio in the PUD is 0.1-99 polyester polyol to 99.9-1 polyether polyol. More preferably, the ratio is 50-70 polyester polyol to 30-50 polyether polyol. The polyester:polyether ratio in the PUD is 1.5:6.5:4.0. More preferably the ratio is 1:5:2.5.

Typically, the ratio of the polyol mixture to the isocyanate is 85:15 to 55:45. More preferably, the ratio is 75:25 to 65:35.

As will be appreciated by those skilled in the art, the order of mixing the aforementioned reagents may be changed.

As used herein, a polyurethane dispersed in water is referred to as a PUD. When a polyurethane is dispersed in water, it is understood that the water optionally further comprises other, additional solvents, such as ketones, C\(_3\)-C\(_6\) alcohols, ethers, polyethers, DMF, dipropylene glycol dimethyl ether, and NMP. The water may contain one or more than one additional solvent. Preferably, these additional solvents comprise less 10% by weight, based on the weight of the water and the additional solvent or solvents. More preferably they comprise less than 5% by weight. Still more preferably, it is less than 1% by weight. Most preferably, non-water solvents are not present in PUD. While deionized and/or distilled water may be used, it is not required.

The leathers and methods of making the leathers disclosed herein, optionally further comprise an additive that is a filler (such as wood fibers, CaCO\(_3\), SiO\(_2\), and TiO\(_2\)), a flame retardant, a pigment, a flowing additive, handle feel additive, antioxidant, anti-UV additive, antistatic agent, antimicrobial agent, or combinations thereof. Wood fibers also include wood flour. In one embodiment, the leathers and methods require the presence of at least one of the aforementioned additives.

The aforementioned fillers, when present, account for 0.1-50% by weight of the composition (excluding the fabric). More preferably, when present, the fillings account for 0.1-40% by weight of the composition. Still more preferably, the fillers account for 0.1-30% by weight of the composition.

The non-additives, i.e., the aforementioned additives, not including the fillers, typically account for 0.01-20% by weight of the composition. More preferably, the non-filler additives account for 0.1-10% by weight of the composition. Still more preferably, the non-filler additives account for 1-5% by weight of the composition. Flowing additives, handle feel additives, antioxidants, anti-UV additives, antistatic agents, and antimicrobial agents are typically comprise less than 5% by weight of the composition. The additives may be added to the polyester polyol modified PUD, to the mixture comprising the polyester polyol modified PUD or combinations thereof.

Examples of suitable surfactants used in the leathers and methods disclosed herein include, cationic, anionic, or nonionic surfactants. Suitable classes of surfactants include, but are not restricted to, sulfates of ethoxylated phenols such as poly(oxy-1,2-ethanediyl)-x-sulfonic acid, (nonylphenoxymethyl)alkyl sulfates, alkali metal fatty acid salts such as alkali metal oleates and stearates; polyoxyalkylene nonionics such as polyethylene oxide, polypropylene oxide, polybutylene oxide, and copolymers thereof; alcohol alkoxylates; ethoxylated fatty acid esters and alkylphenol ethoxylates; alkali
metal lauryl sulfates; amine lauryl sulfates such as triethanolamine lauryl sulfate; quaternary ammonium surfactants; alkali metal alkylbenzene sulfonates such as branched and linear sodium dodecylbenzene sulfonates; amine alkyl benzene sulfonates such as triethanolamine dodecylbenzene sulfonate; anionic and nonionic fluorocarbon surfactants such as fluorinated alkyl esters and alkali metal perfluorooctyl sulfonates; organosilicon surfactants such as modified polydimethylsiloxanes; and alkali metal soaps of modified resins. Exemplary surfactants include sodium octadecyl sulfosucciniminate, sodium dodecylbenzene sulfonate, sodium alpha olefin sulfonate, sodium steareate, cocamidopropyl betaine, and ammonium steareate. Typically the total amount of surfactant used is less than 10%, based on the total weight of the dried synthetic leather. When the surfactant is mixed with the PUD, it is used to stabilize the air bubbles in the frothed PUD. The surfactant or surfactants are sometimes used as a concentrate in water. When two or more surfactants are being used, they may be added to the mixture simultaneously or one after the other.

At least one thickener is added to the PUD before it is frothed. Thickeners are well known in the art and any thickener may be used in the leathers and methods disclosed herein. The thickener may be non-associative or associative. It may be a cellulose ether derivative, natural gum alkali swellable emulsion, a clay, an acid derivative, an acid copolymer, a urethane associate thickener (UAT), a polyether urea polyurethane (PEUPU), a polyether polyurethane (PEPU) or a hydrophobically modified ethoxylated urethane (HEUR). One preferred thickener is based on an acrylic acid copolymer, with ethylene acrylic acid copolymer (which is sold by The Dow Chemical Company as ACUSOL 810A) being particularly preferred. Preferably, the thickener does not cause the PUD containing mixture to become unstable. If desired, a combination of thickeners may be used.

Examples of thickeners include those that do not cause the dispersion to become unstable. More preferably, the rheological modifier is a water soluble thickener that is not ionized. Examples of useful thickeners include methyl cellulose ethers, alkali swellable thickeners (e.g., sodium or ammonium neutralized acrylic acid polymers), hydrophobically modified alkali swellable thickeners (e.g., hydrophobically modified acrylic acid copolymers) and associative thickeners (e.g., hydrophobically modified ethylene-oxide-based urethane block copolymers). Preferably the rheological modifier is a methylcellulose ether. The amount of thickener may be any useful amount. Typically the amount of thickener is at least about 0.1% to about 10% by weight of the total weight of the dispersion. Preferably the amount of thickener is between about 0.5% to about 7% by weight.

Chain extenders are bifunctional or polyfunctional, low molecular weight (typically weighing from 18 up to 500 g/mol) compounds that contain at least two active hydrogen containing groups. Any chain extender known to be useful to those of ordinary skill in the art of preparing polyurethanes can be used in the leathers and methods disclosed herein. Examples of chain extenders include diols, polyols, diamines, polyamines, hydrazides, acid hydrazides, and water. Of these, amine containing chain extenders and water are preferred. Furthermore, one or a combination of chain extenders may be used. For example, the chain extender may be mixed with or otherwise contain water.

Examples of chain extenders include water, piperazine, 2-methylpiperazine; 2,5-dimethylpiperazine; 1,2-di-aminopropane; 1,3-diaminopropane; 1,4-diaminobutane; 1,6-diaminohexane, isophorone diamine, mixtures of isomers of 2,2,4- and 2,4,4-trimethyl hexamethylene diamine, 2-methyl pentamethylene diamine, diethylene triamine, dipropylenetrimine, triethylenetetramine, 1,3- and 1,4-xylylene diamine, aaaaaf-‘tetramethyl-1,3- and -1,4-xylylene diamines and 4,4’-dicyclohexylmethylenediamine, 3,3’-dimethyl-4,4’-dicyclohexylmethylenediamine, 1,2-cyclohexanedi amine, 1,4-cyclohexanediamine, dimethylolurea, hydrazine or adipic acid dihydrazide ethylene glycol; aminos, ethylenolamine (AEEA); aminopropylolamine, aminohexylolamine, aminopropanolamine, amionopropylolproplamine, aminohprylolproplamine; cyclohexane dimethanol; ethanolamine; diethanolamine; piperazine, JEFFAMINE D-230 (a polyether with two amino terminating groups, having a molecular weight of approximately 230 that is sold by the Huntsman Co.), methyl diethanolamine; phenyl diethanolamine; diethylolurediamine, dimethylolurea, trimethyleneolproplamine. Particularly preferred chain extenders include water, AEEA, piperazine and 1,4-diaminobutane.

Examples of pigments, include TiO₂, carbon black and other, known pigments. Pigments are well known in the art and typically present in less than 20% by weight, based on the dried leather.

Examples of flame retardants that may be used in the leathers and methods disclosed herein include those typically used to give enhanced flame retardant properties to a typical latex foam. Such flame retardants include phosphate esters, halogenated phosphate esters or a combination thereof. Representative examples of phosphate esters include dimethyl phosphate (DMMP) and diethyl phosphate (DEEP). Representative examples of phosphates esters include triethyl phosphate and triethyl phosphate. When used the phosphate or phosphate ester flame retardants are present in the final foam at a level of from 0.5 to 30 percent by weight of the final foam.

Representative examples of halogenated phosphate esters include 2-chloroethanol phosphate (C₃H₇Cl₂O₃P); 1-chloro-2-propanol phosphate [tris(1-chloro-2-propyl)phosphate] (C₃H₇Cl₂O₃P); 1,3-Dichloro-2-Propanol Phosphate (C₃H₇Cl₂O₃P) also called tris(1,3-dichloro-2-propyl)phosphite; tri(2-chloroethyl)phosphate; tri(2,2-dichloroisopropyl)phosphite; tri(2,3-dibromopropyl)phosphite; tri(1,3-dichloropropyl)phosphate; tetrakis(2-chloroethyl)ethylene diphosphate; bis(2-chloroethyl) 2-chloroethylphosphonate; diphosphates [2-chloroethyl diphasphite]; tetrakis(2-chloroethyl) ethylene phosphonate; tris(2-chloroethyl)-phosphate, tris(2-chloropropyl) phosphate, tris(2,3-dibromopropyl)-phosphate, tris(1,3-dichloropropyl)phosphite tetrakis(2-chloroethyl-ethylene diphosphate and tetrakis(2-chloroethyl) ethyleneoxyethylene phosphonate. When used as a flame retardant, the halogenated phosphate ester will comprise 0.5 to 30 percent by weight of the final foam.

Dehydratable flame retardants, such as alkali silicates, zeolites or other hydrated phosphates, borosilicates or borates, alumina hydroxides, cyanuric acid derivatives, powdered melamine, graphites, micro, vermiculites, perlites, aluminhydracalcie, hydromagnesite, thiamasite and wermundite. Al₂O₃, H₂O, and Alumina trihydrate, may also be used.

The dehydratable flame retardant is generally added to the polyurethane dispersion in an amount of from 5 to 120
parts per 100 parts dispersion solids of the final Compound. Preferably the flame retardant is added in an amount from 10 to 100 parts per 100 parts dispersion solids of the final Compound. More preferably the flame retardant is added in an amount from 20 to 80 parts per 100 parts dispersion solids of the final Compound.

[0051] Examples of hand feel additives include organic silicon compounds. When present, the amount of hand feel additive is 0.1% to about 10% by weight of the total weight of the dispersion. Preferably the amount of hand feel additive is between about 0.5% to about 5% by weight. In another embodiment, it is less than 3% by weight.

[0052] Antioxidants are known in the art and include polymeric hindered phenol resins.

[0053] In an embodiment according to any of the preceding aspects and/or embodiment(s), the synthetic leathers and methods described herein further comprise at least one additive that is CaCO₃, SiO₂, wood fibers, TiO₂, or combinations thereof.

[0054] In another embodiment of any of the previously described aspects and/or embodiments, the mixture further comprises at least one additive that is a flame retardant, a pigment, a flowing additive, hand feel additive, antioxidant, anti-UV additive, or combinations thereof. Typically, these additives comprise 0.01 to 10% by weight of the solid content. More preferably, these additives comprise 0.1-8% by weight (still more preferably, 2-5%) of the solid content.

[0055] Frothing may be accomplished by any method known in the art. Examples include mechanical mixing, bubbling a gas into the mixture or a combination thereof.

[0056] Likewise, applying the frothed mixture to the fabric may also be accomplished by any method known in the art.

[0057] The synthetic leathers and methods described herein utilize a fabric that is coated with the frothed mixture. Many different fabrics that are known in the art may be used. The fabric may be woven or non-woven. In one embodiment, the fabric is a non-woven fabric. The fabric may be made by any suitable method such as those known in the art. The fabric may be prepared from any suitable fibrous material, such as, but not limited to, synthetic fibrous materials and natural or semi synthetic fibrous materials and mixtures or blends thereof. Examples of synthetic fibrous materials include polyesters, polyamides, polyacrylates, polylefins, polyvinyl chloride, polyvinylidene chloride, polyvinyl alcohols and blends or mixtures thereof. Examples of natural semi-synthetic fibrous materials include cotton, wool and hemp.

[0058] One preferred fabric is needle cotton and polyester fiber hybrid woven fabric having short fibers (less than 1 mm) on the surface.

[0059] Another preferred fabric is needle cotton and polyester fiber hybrid woven fabric having long (greater than 3 mm) fibers on the surface.

[0060] In the leathers and methods disclosed herein, the fabric is optionally impregnated with a polymer resin. Acceptable resins include isocyanate containing resins, such as polyisocyanates (which contain at least two isocyanate groups) were discussed above.

[0061] The impregnation of the fabric may be conducted by any suitable method known in the art. Examples include dipping, spraying or doctor blading. After impregnating, the impregnated textile may have excess resin removed to leave the desired amount of dispersion within the textile. Typically, this may be accomplished by passing the impregnated textile through rubber rollers.

[0062] Generally, the impregnated fabric is impregnated with a resin in an organic solvent (which makes a solution) or water (which makes a dispersion). Typical solvents include dimethylformamide (DMF), methylethyl ketone (MEK) and toluene, although other solvents will afford acceptable results. Generally, the organic solvent used to impregnate the fabric will contain 0.5-50% by weight of resin. More preferably, the organic solvent will contain 5-30% by weight of resin. Still more preferably, 15-25% by weight of resin.

[0063] If the fabric is impregnated with a resin in an organic solvent, then typical solvents include dimethylformamide (DMF), methylethyl ketone (MEK) and toluene, although other solvents will afford acceptable results. Generally, the organic solvent used to impregnate the fabric will contain 0.5-50% by weight of resin. More preferably, the organic solvent will contain 5-30% by weight of resin. Still more preferably, 15-25% by weight of resin.

[0064] The frothed mixture may be applied to the fabric using any suitable method known in the art. Examples include using a Labcoater type LTE-5 (Werner Mathic AG).

[0065] Likewise, the thickness of the froth on the fabric can be adjusted using methods known in the art. Examples include using a doctor blade assembly.

[0066] The methods require drying or otherwise treating/ curing the coated fabric (i.e., the optionally impregnated fabric that is coated with the frothed mixture) so that the synthetic leather forms. Suitable drying conditions include subjecting the froth coated fabric to 1) a constant temperature until dry, 2) a temperature gradient wherein the temperature changes over time, or 3) a multistep drying regime where the temperature is held for a set amount of time and then changed to a different temperature, which is then held for a set amount of time (3, 4, 5, or more drying steps may also be used). The drying time for each step may be the same or different. Typical drying times are from a few seconds up to one hour. One example of a suitable drying protocol is to subject the froth covered, optionally impregnated fabric to a temperature that is at least 80°C and no more than 250°C. More preferably, the optionally impregnated fabric is heated to a temperature of 50-105°C for 4-10 minutes and then to a temperature of 165-175°C for 3-10 minutes. During the drying process, the water evaporates and the polyolefin sets (which may include melting of at least some of the material coated onto the fabric) and thereby forms the final coating. The drying process should not cause decomposition of any of the synthetic leather components.

[0067] Typically, the drying is performed in an oven at atmospheric pressure, but it can be performed at pressures above or below atmospheric pressure.

[0068] In one embodiment, the polyester polyol modified PUD, the filler or fillers, and the other additives comprise 0.1-99.9% by weight of the total composition. More preferably, they comprise 60-99.9% by weight of the total composition. Still more preferably, 70-99.9% by weight of the total composition.

General Procedure for the Preparation of PUD Based, Poromeric Synthetic Leather

Preparation of the Prepolymer:

[0069] Put at least one isocyanate resin into the reactor. If a resin is a solid, heat it until it is melted.

[0070] Combine the polyols in a separate reaction vessel. If the polyol mixture is a solid at ambient temperature, heat the
polyol mixture to a temperature higher than the mixture’s melting point. Adjust the net-controlled polymerization rate (CPR) to be lower than -10 using a scavenger compound, such as benzyl chloride. Combine the polyol mixture and the isocyanate(s). Stir and heat the combined mixture. Test the NCO% periodically using ASTM method ASTM D 2572-87. When the desired NCO content is reached, reduce the temperature of the reaction mixture.

Preparation of the Polyurethane Dispersion (PUD):

[0071] The prepolymer (from above) was placed in a plastic jar. The jar was secured and a Cowles blade was inserted into the prepolymer such that the blade is just covered. At least one surfactant is added to the prepolymer, with mixing at 3000 rpm. Cold (~5° C) deionized water (DI water) is slowly added to the mixture. Gradually, the water-in-oil emulsion is converted into an oil-in-water dispersion. A solution of chain extender in DI water is slowly fed into the dispersion, the final dispersion is allowed to degas under ambient condition with random stirring.

Experimental Procedures

[0072] The following three PUDs were used in the examples.

<table>
<thead>
<tr>
<th>TABLE 1</th>
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<tbody>
<tr>
<td>Type</td>
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<tr>
<td>Materials</td>
</tr>
<tr>
<td>Company</td>
</tr>
<tr>
<td>Solid content/%</td>
</tr>
<tr>
<td>Polyester/ Polyether/</td>
</tr>
<tr>
<td>Isocyanate Ratio</td>
</tr>
</tbody>
</table>

[0073] Note: PUD 1 is the control because it does not contain any polyester polyol. PUDs 2 and 3 contain polyester polyol and were made according to the methods described herein. The polyester in PUD 2 was Bester 127 (a polyester polyol having Mn of about 2,000, sold by The Dow Chemical Company), and the polyester in PUD 3 was Bester 48 (a polyester polyol product with an Mn=1000, sold by The Dow Chemical Company). The polyethers in all these three PUDs were mainly VORANOL 9287A (a 2000 molecular weight, 12 percent ethylene oxide capped diol stabilized with allyldiphenylamine, a product of The Dow Chemical Company) with some small dosage polyether resins (Mn=approximately 2000, sold by The Dow Chemical Company) and CARBO-WAX™ Methoxy polyethylene Glycol (MPEG) 1000 (from The Dow Chemical Company) mixture. The isocyanate was 4,4'-Methylene diphenyl disiocyanate (MDI) from Huntsman.

[0074] The following two fabrics were used in the examples below.

<table>
<thead>
<tr>
<th>TABLE 2</th>
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<tbody>
<tr>
<td>Fabric type</td>
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<tr>
<td>Fabric 1</td>
</tr>
<tr>
<td>Fabric 2</td>
</tr>
</tbody>
</table>

[0075] Preparation of the Control Samples:

[0076] A porous mic of the synthetic leather was made using frothed PUD. The frothing PUD dispersion had a solids content of 50-55 percent by weight with ammonium stearate (STANFAX 320, Para-chem), disodium octadecyl sulfosuccinimide (STANFAX 318, Para-chem), cocamidopropyl betaine (STANFAX 590, Para-chem) and acrylic acid copolymer thickener (ACUSOL 810A, Dow). The thickened PUD viscosity was controlled to 13,000 cp to 28,000 cp. The detailed PUD formulations appear in Table 3.

[0077] The PUD was frothed using a Model 2MT1A foam machine (E. T. HANKES Corp.) run at 1000 rpm. The wet froth density of the PUD was about 0.50-0.85 g/cm³. A Labcoaster type LTE-S (Werner Mathis AG) was used to apply the frothed PUD to a fabric that was attached to pin frame. The doctor knife was positioned at 1.8-2.5 mm between the roller and knife (including resin and fabric). The frothed dispersion was dispersed and the doctor bladed to foam a coating of frothed PUD on the fabric. The coated fabric was then placed in an oven at 100°C for 6-10 min, which was then heated to 170°C in about 5 min. to form the synthetic leather having a porous mic.

<table>
<thead>
<tr>
<th>TABLE 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>PUD porous mic layer formulation</td>
</tr>
<tr>
<td>Items</td>
</tr>
<tr>
<td>Materials</td>
</tr>
<tr>
<td>Fabric type</td>
</tr>
<tr>
<td>PUD 1 (Syntegra 3000)</td>
</tr>
<tr>
<td>Stanfix 320</td>
</tr>
<tr>
<td>Stanfix 590</td>
</tr>
<tr>
<td>Stanfix 318</td>
</tr>
<tr>
<td>Acusol 810A</td>
</tr>
<tr>
<td>Viscosity/cp</td>
</tr>
<tr>
<td>Foam density/(g/cm³)</td>
</tr>
</tbody>
</table>

[0078] Preparation of the Experimental Examples

[0079] The polyester polyol modified PUD based leathers were made essentially according to the methods described above for the control samples. The key difference being the use of the formulations and fabrics in Table 4 replacing those in Table 3.
TABLE 4 Polyester modified PUD poromeric layer formulation

<table>
<thead>
<tr>
<th>Materials</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
<th>Sample 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fabric type</td>
<td>Fabric 1</td>
<td>Fabric 2</td>
<td>Fabric 3</td>
<td>Fabric 4</td>
</tr>
<tr>
<td>PUD 2</td>
<td>1000</td>
<td>750</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stanfac 320 (ammonium stearate)</td>
<td>40.0</td>
<td>30.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stanfac 590 (octadecyl betaine)</td>
<td>11.3</td>
<td>10.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stanfac 318 (dodecyl octadecyl sulfosuccinate)</td>
<td>13.1</td>
<td>9.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acryl 810A (acrylic acid copolymer)</td>
<td>76.5</td>
<td>77.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Viscosity (cp)</td>
<td>17500</td>
<td>17200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Foam density (g/cm³)</td>
<td>0.781</td>
<td>0.622</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Peel Strength Test:

Peel strength tests were conducted according to the GB/T 8949-2008 Chinese Standard. Briefly, the synthetic leather was cut into two 15 cm x 12 cm leather sheets. Then these two leather sheets were glued together using a suitable adhesive, but about 5 cm (in the length direction) was not treated with adhesive. The two pieces were pressed with a 5 Kg steel plate, dried and cured over 24 hours. The bonded sheet was cut along the length-wise into four 15 cm x 3 cm samples. These four samples were tested using an Instron machine with a speed of 200 cm/min.

PUD Viscosity Measurement

Bulk viscosities of the thickened PUD before frothing were measured using a Brookfield viscometer with a 20 rpm #6 spindle.

Results of Leather Peel Strength:

Peel strength of the poromeric layer samples

<table>
<thead>
<tr>
<th>Items</th>
<th>Control 1</th>
<th>Control 2</th>
<th>Sample 1</th>
<th>Sample 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peel strength (N/(3 cm))</td>
<td>28</td>
<td>46</td>
<td>52</td>
<td>90</td>
</tr>
<tr>
<td>Fabric</td>
<td>Fabric 1</td>
<td>Fabric 2</td>
<td>Fabric 1</td>
<td>Fabric 2</td>
</tr>
</tbody>
</table>

The peel strength increased from 28 N/(3 cm) (Control 1) to 46 N/(3 cm) (Control 2) by changing from a fabric having long fibers on the surface to a fabric having short fibers on the surface. Replacing the PUDs in Control samples 1 and 2 with polyester polyol modified PUD (Sample 1 and 2) afforded synthetic leathers having significantly improved peel strengths, relative to PUDs that do not contain any polyester polyol modified PUD.

Comparing Control 1 to Sample 1 shows the polyester polyol modified PUD has a peel strength that is 85% higher than the corresponding non-modified PUD. Likewise, Sample 2 has a peel strength that is 96% higher than the corresponding non-modified PUD.

FIG. 1 (Control 1) and 3 (Example 1), both are cross sections of synthetic leathers on fabrics having long fibers, and they have similar structures. Thus, Example 1, while having superior properties relative to Control 1, has a similar overall structure. The same applies for FIG. 2 (Control 2) and 4 (Example 2), but the fabrics contain short fibers.

What is claimed is:

1. Methods for producing externally stabilized, poromeric synthetic leathers having improved peel strength, the methods comprising:

   1. Preparing a prepolymer from a mixture comprising at least one polyester polyol, at least one polyether polyol, at least one isocyanate and optionally in a solvent;
   2. Mixing the prepolymer, water, and a first surfactant;
   3. Optionally add a second chain extender to form a PUD;
   4. Preparing a mixture comprising said PUD, at least one surfactant, and at least one thickener;
   5. Frothing said mixture;
   6. Applying the frothed mixture to a fabric and thereby forming a coated fabric;
   7. Adjusting the thickness of the frothed mixture on the coated fabric;
   8. Drying the coated fabric.

2. Methods of improving the peel strength of poromeric synthetic leathers, the methods comprising:

   1. Preparing a prepolymer from a mixture comprising at least one polyester polyol, at least one polyether polyol, at least one isocyanate and optionally in a solvent;
   2. Mixing the prepolymer, water, and a first surfactant;
   3. Optionally add a second chain extender to form a PUD;
   4. Preparing a mixture comprising said PUD, at least one surfactant, and at least one thickener;
   5. Frothing said mixture;
   6. Applying the frothed mixture to a fabric and thereby forming a coated fabric;
   7. Adjusting the thickness of the frothed mixture on the coated fabric;
   8. Drying the coated fabric.

3. Methods according to claim 1, wherein the mixture comprises at least two surfactants.

4. Methods according to claim 1, wherein at least one surfactant is ammonium stearate, disodium octadecyl sulfosuccinate or cocamidopropyl betaine.

5. Methods according to claim 1, wherein the mixture comprises at least two surfactants.

6. Methods according to claim 1, wherein the mixture further comprises at least one additive that is CaCO₃, SiO₂, wood fibers, TiO₂, a flame retardant, a pigment, a flowing additive, a handle additive, an antioxidant, anti-UV additive or combinations thereof.

7. Methods according to claim 1, wherein the PUD has a solid content of 50-65% by weight.

8. Methods according to claim 1, wherein the isocyanate comprises isophorone disiocyanate, 4,4'-diisocyanatodiphenylmethane, 2,4'-diisocyanatodiphenylmethane, or combinations thereof.

9. Methods according to claim 1, wherein the polyester: polyether ratio in the PUD is 1:0.5-4.

10. Methods according to claim 1, wherein the coated fabric is dried/cured at a temperature of at least 30°C and no more than 200°C.

11. Methods according to claim 1, wherein the isocyanate comprises methylenediphenyl disiocyanate, and at least one polyester polyol has an Mn of 1000-2000.

12. Methods according to claim 1, wherein the thickening agent is an acrylic acid copolymer.

13. Methods according to claim 1, wherein the PUD is mixed with at least three surfactants that are independently selected from the group consisting of disodium octadecyl sulfosuccinate, sodium dodecyl benzene sulfonate, sodium alpha olein sulfonate, sodium stearate, cocamidopropyl betaine, and ammonium stearate.
14. Methods according to claim 13, wherein the at least three surfactants are ammonium stearate, disodium octadecyl sulfosuccinate and cocamidopropyl betaine, and are in the ratio of 1:0.2-0.4:0.23–0.4.

15. A porometric synthetic leather made according to claim 15.