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(54) **Title**: A POLYURETHANE COMPOSITION AND THE PROCESS OF REPAIRING POLYURETHANE BALLAST BED BY USING THE SAME

(57) **Abstract**: The present invention relates to a polyurethane composition for repairing polyurethane ballast bed, comprising: amine initiated polyether polyol, short chain polyether polyol and long chain polyether polyol. The polyurethane foam prepared from the polyurethane composition has favorable tensile strength and hardness, and can be used to support sleepers so as to repair settling polyurethane ballast bed.

A polyurethane composition and the process of repairing polyurethane ballast bed by using the same

Field

[0001] The present invention relates to a polyurethane composition for repairing polyurethane ballast beds, and the process of repairing ballast bed by using the same.

Background

[0002] A railway track bed usually refers to a ballast layer laid beneath sleepers and above a roadbed, which serves as a basis for a track frame and is mainly used to support sleepers and to distribute a massive railway vehicle load transferred from the steel rail and sleepers evenly to a surface of the track bed, thereby reducing deformation of the roadbed and ensuring traffic safety. A railway track bed having ballast layer is also referred to as a ballast bed. In addition, ballast beds also offer buffering and vibration-reducing effect, and have good versatility and low construction cost, thus they have been widely used in the industry.

[0003] When high speed and heavy loaded train passes, the heavy load will be transformed to substantial impact to the ballast beds through rails and sleepers. To prevent collision, disposition, crush and desertification of the ballasts, the track bed is often reinforced by polyurethane foam. When polyurethane is injected to a ballast bed, it rapidly penetrates to the voids among ballasts, and forms a composite structure comprising ballasts as matrix and polyurethane foams filling the voids after curing. The ballast bed having this composite structure is particularly suitable to bear high speed and heavy loaded trains, because it has high loads and high impact energy absorbing characteristics, high durability and high resilience under dynamic loads.

[0004] However, polyurethane ballast beds may suffer settlement after used for a period of time under dynamic loads, immersed in water or with natural subground settlement. In order to ensure polyurethane ballast bed functions well to spread the load and improve the track vertical and horizontal resistance and elasticity, the settled ballast bed must be repaired.

[0005] Existing repairing method mainly uses a stamping machine to lift the track up. However, the stamping machine cannot be applied to polyurethane ballast

bed which has been stabilized by polyurethane foam.

[0006] Therefore, a repairing method is needed for repairing settled polyurethane ballast beds.

Summary

[0007] In one aspect, the present invention provides a polyurethane composition for repairing polyurethane ballast bed, comprising:

(a) one or more polyisocyanate;

(b) a polyether polyol mixture comprising:

(b1) a first polyether polyol selected from amine initiated polyether polyols having a functionality of 2-6 and a hydroxyl number of 10-1200 mg KOH/g;

(b2) a second polyether polyol selected from polyol initiated polyether polyols having a functionality of 2-3 and a hydroxyl number of 12-120 mg KOH/g;

(b3) a third polyether polyol selected from polyol initiated polyether polyols having a functionality of 3-8 and a hydroxyl number of 150-1200 mg KOH/g;

Wherein the first polyether polyol has an amount of 10-60 wt. %, the second polyether polyol has an amount of 1-70 wt. %; the third polyether polyol has an amount of 10-70 wt. %, based on 100 % by weight of the polyether polyol mixture.

[0008] In one embodiment of the present invention, the first polyether polyol has a functionality of 4-6 and a hydroxyl number of 300-1000 mg KOH/g; preferably, the first polyether polyol has a functionality of 4 and a hydroxyl number of 400-800 mg KOH/g; more preferably, the first polyether polyol has an amount of 30-60 wt.%, based on 100 % by weight of the polyether polyol mixture.

[0009] In another embodiment of the present invention, the second polyether polyol has a functionality of 2-3 and a hydroxyl number of 25-60 mg KOH/g; preferably, the second polyether polyol is 10-30 wt.%, based on 100 % by weight of the polyether polyol mixture.

[0010] In still another embodiment of the present invention, the third polyether polyol has a functionality of 3-6 and a hydroxyl number of 150-900 mgKOH/g; preferably the third polyether polyol has a functionality of 3-5 and a hydroxyl number of 250-700 mgKOH/g; more preferably, the third polyether polyol has an amount of 30-50 wt.%, based on the 100 % by weight of the polyether polyol mixture.

[0011] In yet another embodiment of the present invention, the polyisocyanate is one or more selected from the group consisting of the diphenylmethane diisocyanate, toluene diisocynate or the combination thereof.

[0012] In another aspect, the present invention provides a process for repairing settled polyurethane ballast beds, wherein the sleepers for supporting the track are disposed on the ballast bed, and the process comprising the step of injecting the polyurethane composition mentioned above to the void between the sleepers and the surface of the polyurethane ballast bed such that the polyurethane composition is cured to fill the void.

[0013] In one embodiment of the present invention, the void between the sleepers and the surface of the polyurethane ballast bed is formed by lifting the track to a preset position; preferably the void between the sleepers and the surface of the polyurethane ballast bed has a height of about 10-100 mm.

[0014] In one embodiment of the present invention, the process further comprises the step of applying reinforcement material; preferably the reinforcement material is the one or more selected from the group consisting of alkali-free glass fabric, non-woven fabric, textile, glass fiber, carbon fiber, aramid fiber, stones, bricks, concrete blocks, metal blocks, rubber particles, plastic particles, yellow sand, glass bead and the combination thereof.

[0015] In still another aspect, the present invention provides a railway system, comprising sleepers and polyurethane ballast bed, wherein a polyurethane foam prepared from the polyurethane composition mentioned above is disposed between the sleepers and the polyurethane ballast bed to support the sleepers.

[0016] In one embodiment of the present invention, the polyurethane foam has a thickness of 10-100 mm.

[0017] In another embodiment of the present invention, the polyurethane foam has a tensile strength of 2-40 Mpa, and a hardness of 30-90 Shore A and 40-80 shore D.

[0018] In still another embodiment of the present invention, the polyurethane foam has a density of 1.5 g/cm^3 and an elongation at break of 2-55 %.

Detailed Description

Polyurethane composition

[0019] In one aspect, the present invention provides a polyurethane composition for repairing polyurethane ballast bed, comprising:

(a) one or more polyisocyanate;

(b) a polyether polyol mixture comprising:

(b1) a first polyether polyol selected from amine initiated polyether polyols having a functionality of 2-6 and a hydroxyl number of 10-1200 mg KOH/g;

(b2) a second polyether polyol selected from the polyol initiated polyether polyols having a functionality of 2-3 and a hydroxyl number of 12-120 mg KOH/g;

(b3) a third polyether polyol selected from polyol initiated polyether polyols having a functionality of 3-8 and a hydroxyl number of 150-1200 mg KOH/g;

Wherein the first polyether polyol has an amount of 10-60 wt. %, the second polyether polyol has an amount of 1-70 wt. %; the third polyether polyol has an amount of 10-70 wt. %, based on 100 % by weight of the polyether polyol mixture.

[0020] The polyurethane composition of the present invention doesn't comprise additional small molecule catalysts. Therefore the polyurethane composition doesn't cause pollution after being applied to the ballast bed. Moreover, the prepared polyurethane foam has similar or even better hardness and mechanical strength compared to sleepers, therefore can support the sleepers and fix the settled polyurethane ballast bed.

[0021] The polyurethane composition of the present invention may be one component composition or multi-component composition, preferably two-component composition. The two-component polyurethane composition may comprise component A which mainly comprises polyisocyanates, and component B which comprises polyether polyol mixture.

[0022] Component A comprises one or more polyisocyanates. The polyisocyanates may be described by the formula, R(NCO)n, wherein n = 2-4, and R represents an aliphatic hydrocarbon radical containing 2-18 carbon atoms, an aromatic hydrocarbon radical containing 6-15 carbon atoms, or an araliphatic hydrocarbon radical containing 8-15 carbon atoms.

[0023] Suitable examples of the polyisocyanates include but not limited to ethylene diisocyanate, 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate (HDI), 1,2-dodecane diisocyanate, cyclobutane-1,3-diisocyanate, cyclohexane 1,3- and 1,4-diisocyanates, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethyl-cyclohexane, 2,4- and 2,6-hexahydrotoluene diisocyanates, hexahydro-1,3- and 1,4-phenylene diisocyanate, perhydro-2,4- and 4,4'-diphenylmethane diisocyanate, 1,3-and

1,4-phenylene diisocyanate, 1,4-durol diisocyanate, 4,4'-stilbene diisocyanate, 3,3'-dimethyl-4,4'-biphenylene diisocyanate, toluene 2,4- and 2,6-diisocyanates (TDI) and any mixtures of these two isomeric compounds, diphenylmethane-2,4'-, 2,2'- and 4,4'-diisocyanates (MDI), and naphthylene-1,5-diisocyanate (NDI), their isomers and the combination thereof. The polyisocyanate is preferably selected from methylene diphenyl diisocyanate, toluene diisocyanate or the combination thereof, more preferably methylene diphenyl diisocyanate.

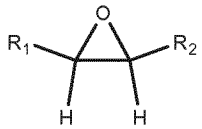
[0024] The polyisocyanates also include the modifications of the above mentioned isocyanates containing carbodiimide, uretoneimine, allophanate or isocyanurate structures, preferably methylene diphenyl diisocyanate modified by methylene diphenyl diisocyanate or carbodiimide, their isomers and the combination thereof.

[0025] The polyisocyanates can also be prepolymers produced by the common process known in the prior art. The prepolymer preferably has a NCO content of 8-50 wt.%, more preferably 10-33 wt.%.

[0026] Component B comprises polyether polyol mixture (b) which comprises amine initiated polyether polyol (the first polyether polyol), and long chain polyether polyol (the second polyether polyol) and short chain polyether polyol (the third polyether polyol) prepared from polyols as starter.

[0027] The first polyether polyol is prepared from amine as a starter and epoxy compounds.

[0028] As used herein, the term "epoxy compound" refers to the compound having the following formula (I):



(I)

[0029] Wherein R_1 and R_2 are independently selected from the group consisting of H, C_1-C_6 straight chain or branch chain alkyl, and phenyl and substituted phenyl.

[0030] It is well known to a person skilled in the art for the preparation process of the "epoxy compound", for example prepared by the oxidation of alkene.

[0031] Examples of epoxy compound suitable for use in the present invention include, but not limited to, ethylene oxide, 1,2-propylene epoxide, 1,2-butylene oxide, 2,3-butylene oxide, phenylethylene oxide or the combination thereof.

[0032] As used herein, the term "epoxy compound" further comprises oxacycloalkane, such as, but not limited to, tetrahydrofuran and oxetane.

[0033] As used herein, the "amine" refers to the compounds comprising primary amine

group, secondary amine group, tertiary amine groups or the combination thereof. The examples of amine suitable for use in the present invention include, but not limited to triethanolamine, ethylene diamine, toluene diamine, diethylene triamine, triethylene tetramine and the derivates thereof, preferably ethylene diamine or toluene diamine.

[0034] The first polyether polyol suitable for use in the present invention may be selected from the group consisting of: the polyether polyols prepared from the ring-opening polymerization of ethylene diamine as starter and propylene oxide, the polyether polyols prepared from the ring-opening copolymerization of ethylene diamine as starter and propylene oxide and ethylene oxide, the polyether polyols prepared from the ring-opening polymerization of toluene diamine as starter and propylene oxide, the polyether polyols prepared from the ring-opening polymerization of toluene diamine as starter and propylene oxide and terminated with ethylene oxide, the polyether polyols prepared from the ring-opening polymerization of toluene diamine as starter and ethylene oxide and terminated with propylene oxide.

[0035] In one embodiment of the present invention, the first polyether polyol has a functionality of 2-6, and a hydroxyl number of 300-1000 mgKOH/g, preferably a functionality of 4 and a hydroxyl number of 400-800 mgKOH/g。

[0036] The method of determining hydroxyl number is well known to a person skilled in the art, for example the method disclosed in Houben Weyl, Methoden der Organischen Chemie, vol. XIV/2 Makromolekulare Stoffe, p.17, Georg Thieme Verlag; Stuttgart 1963, the disclosure of which is incorporated by reference in its entirety herein.

[0037] The first polyether polyol may have an amount of 10-90 wt.%, preferably 30-60 wt.%, based on 100% by weight of the polyether polyol mixture.

[0038] Examples of the first polyether polyol suitable for use in the present invention include, but not limited to, GR 403 (ethylene diamine as starter, hydroxyl number 760 mgKOH/g), GR 405(ethylene diamine as starter, hydroxyl number 400 mgKOH/g), GNT-400 (the mixture of toluene diamine and triethanolamine as starter, hydroxyl number 400 mgKOH/g) commercial available from SINOPEC Shanghai Gaoqiao Company, and Desmophen 4050 E (ethylene diamine as starter, hydroxyl number 620 mgKOH/g) and Desmophen 4051 B (ethylene diamine as starter, hydroxyl number 470 mgKOH/g) commercial available from Bayer material Science.

[0039] The second polyether polyol is prepared from polyhydric alcohols as starter and epoxy compounds. As used herein, the “polyhydric alcohol” refers to the compounds having at least two hydroxyls and a hydroxyl number of 10-120

mgKOH/g, the hydroxyl include primary, secondary and tertiary hydroxyl and the combination thereof. Example of the polyols suitable for use in the present invention include, but not limit to ethyleneglycol, diethyleneglycol, triethyleneglycol, tetraethyleneglycol, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 3-methyl-1,5-pentanediol, 1,5-pentanediol, 1,6-hexanediol, 1, 10-decanediol, glycerine, 1,2,4-butanetriol, 1,2,5-pentanetriol, 1,3,5- pentanetriol, 1,2,6-hexanetriol, 1,2,5-hexanetriol, 1,3,6-hexanetriol, trimethylolbutane, trimethylolpropane or di(trimethylolpropane), trimethylolethane, pentaerythritol or dipentaerythritol. The epoxy compound is defined as above.

[0040] In one embodiment of the present invention, the second polyether polyol has a functionality of 2-3, and a hydroxyl number of 10-120 mgKOH/g; preferably a functionality of 2-3, and a hydroxyl number of 20-80 mgKOH/g; more preferably a functionality of 2-3, and a hydroxyl number of 25-60 mgKOH/g. The second polyether polyol has an amount of 1-70 wt.%, preferably 10-30 wt.%, based on 100% by weight of the polyether polyol mixture.

[0041] Examples of the second polyether polyol suitable for use in the present invention include, but not limited to: Arcol 1021 (propylene glycol initiated, hydroxyl number 56 mgKOH/g), Arcol 1011 (propylene glycol initiated, hydroxyl number 112 mgKOH/g), Arcol 1026 (propylene glycol initiated, hydroxyl number 28 mgKOH/g), Arcol 1032 (propylene glycol initiated, hydroxyl number 35 mgKOH/g), Arcol 3553 and Arcol 1053 (glycerol initiated, hydroxyl number 35 mgKOH/g) and Arcol 1362(glycerol initiated, hydroxyl number 28 mgKOH/g), Arcol 5603 and Arcol 5613 (glycerol initiated, hydroxyl number 54 mgKOH/g), all commercial available from Bayer Material Science, and GE 210(propylene glycol initiated, hydroxyl number112 mgKOH/g), GE 220 (propylene glycol initiated, hydroxyl number 112 mgKOH/g), GE 330 (glycerol initiated, hydroxyl number 35 mgKOH/g), all commercial available from SINOPEC Shanghai Gaoqiao Company。

[0042] The third polyether polyol is prepared from polyhydric alcohol as starter and epoxy compound. As used herein, the “polyhydric alcohol” and the “epoxy compound” is defined as above.

[0043] In one embodiment of the present invention, the third polyether polyol has a functionality of 3-8, a hydroxyl number of 150-1000 mgKOH/g, preferably a functionality of 3-6, and a hydroxyl number of 150-900 mgKOH/g, more preferably 3-5, and a hydroxyl number of 250-700 mgKOH/g. The third polyether polyol has an amount of 10-90 wt.%, preferably 10-70 wt.%, more preferably 30-50 wt.%,

based on 100% by weight of the polyether polyol mixture.

[0044] Examples of the third polyether polyol suitable for use in the present invention include, but not limited to: GE 303 (glycerol initiated, hydroxyl number 480 mgKOH/g), GR 635s (sorbitol and glycerol initiated, hydroxyl number 500 mgKOH/g), GSU -450L (sucrose and glycerol initiated, hydroxyl number 435 mgKOH/g), GMN -450 (glycerol initiated, hydroxyl number 450 mgKOH/g), all commercial available from SINOPEC Shanghai Gaoqiao Company, and Desmophen 3601 (sucrose and glycerol initiated, hydroxyl number 260 mgKOH/g), Desmophen 21AP27(sucrose and glycol initiated, hydroxyl number 440 mgKOH/g).

[0045] Besides above mentioned polyether polyol mixture, component B may further comprise one or more high molecular weight polyols, for example, polyester polyol, polycarbonate polyol and polymer polyol, which are added to the composition according to the actual needs. These high molecular weight polyols may have an amount of 1-30 wt.%, based on 100% by weight of the polyurethane composition.

[0046] Suitable polyester polyols may be produced from the reaction of organic dicarboxylic acids or dicarboxylic acid anhydrides with polyhydric alcohols. Suitable dicarboxylic acids are preferably aliphatic carboxylic acids containing 2 to 12 carbon atoms, for example, succinic acid, malonic acid, glutaric acid, adipic acid, suberic acid, azelaic acid, sebacic acid, decane-dicarboxylic acid, maleic acid, fumaric acid, phthalic acid, isophthalic acid, terephthalic acid, and the mixture thereof. Suitable anhydrides are, for example, phthalic anhydride, terachlorophthalic anhydride, and maleic anhydride. Representative polyhydric alcohols include ethanediol, diethylene glycol, 1,2- and 1,3-propanediols, dipropylene glycol, 1,3-methylpropanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, neopentyl glycol, 1,10-decanediol, glycerol, trimethylol-propane, or mixtures of at least two of these diols. Polyester polyols of lactones, for example, ε-caprolactone, can also be used.

[0047] The polycarbonate polyol is preferably polycarbonate diols which may be prepared by the reaction of diols and dialkyl or diaryl-carbonates. The diols are preferably, but not limited to, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, diethylene glycol, trioxymethylene glycol and their mixtures. The dialkyl or diaryl-carbonates are preferably, but not limited to, diphenyl carbonate.

[0048] The polymer polyols are the stable dispersions formed by dispersing solid enhanced particles in polyols liquid. Any polymer polyol (or dispersion) known in

the art can all be included in the polyol component of the present invention, including but not limited to SAN polymer polyol, PHD polymer polyol, PIPA polymer polyol. SAN polymer polyols are obtained by in-situ polymerization of the mixture of acrylonitrile and styrene in basic polyols, PHD polymer polyol are obtained by in-situ polymerization of the isocyanate mixture and diamine in basic polyols, and PIPA polymer polyols are obtained by in-situ polymerization of the isocyanate mixture and diol and/or diol-amine in basic polyol.

[0049] The chain extenders typically are selected from active hydrogen atoms comprising compounds with molecular weights lower than 800, preferably from 18 to 400. The active hydrogen atoms comprising compounds are preferably, but are not limit to alkanediols, dialkylene glycols, and polyalkylene polyols and their mixtures. The examples are ethanediol, 1,4-butanediol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, diethylene glycol, dipropylene glycol, polyoxyalkylene glycols or the mixture thereof. Other suitable substances are branched chain and unsaturated alkanediols such as 1,2-propanediol, 2-methyl-1,3-propanediol,2,2-dimethyl-1,3-propanediol, 2-butyl-2-ethyl-1,3-propanediol, 2-butene-1,4-diol and 2-butyne-1,4-diol, alkanolamines and N-alkyldialkanolamines such as ethanolamine, 2-aminopropanol and 3-amino-2,2-dimethylpropanol, N-methyl and N-ethyl-diethanolamines, as well (cyclo) aliphatic and aromatic amines, e.g. 1,2 ethylenediamine, 1,3-propylenediamine, 1,4-butylenediamine, 1,6-hexamethylenediamine,isophoronediamine, 1,4-cyclohexamethylenediamine, N,N'-diethyl-phenylenediamine, and 2,4 and 2,6 diaminotolune. The chain extender dosage is 0-20 wt.%, based on 100% by weight of the B component.

[0050] Optionally, the polyurethane composition may further comprise blowing agent. The blowing agents may be any conventional physical foaming agent and chemical foaming agent, including but not limited to water, halohydrocarbons, and hydrocarbons. Examples of halohydrocarbons are monochlorodifuloromethane, dichloromonofluoromethane, dichlorofluoromethane, and trichlorofluromethane or the mixture thereof. Examples of hydrocarbons include but not limit to butane, pentane, cyclopentane, hexane, cyclohexane, heptane and the mixture thereof. The blowing agent is most preferably water. The amount of the blowing agent depends on the desired density of ballast layer filled by the polyurethane, preferably 0.3-4.5 wt.%, more preferably 0.5-3.6 wt.%, most preferably 0.6-3.2 wt.%, based on 100% by weight of all the polyols in the polyurethane reaction system (both including the

polyols used as reaction component, and those used as chain extender and other components).

[0051] The B component can optionally comprise catalyst, surfactant and flame retardant and the like.

[0052] The catalyst is preferably, but not limit to, amines and organic metal compounds and their mixtures. The amine catalyst is preferably, but not limit to, triethylamine, tributylamine, triethylene diamine, N-ethylmorpholine, N,N,N',N'-tetramethyl-ethylenediamine, pentamethyl diethylene-triamine, N,N-methylaniline, N,N-dimethylaniline and mixtures thereof. The organic metal catalyst is preferably, but not limit to, stannous diacetate, stannous dioctoate, stannous diethylhexoate, and dibutyltin diacetate, dibutyltin dilaurate, dituty1tin maleate, and dioctyltin diacetate and mixtures thereof. The catalyst dosage is 0.001-10wt.%, based on 100% by weight of the B component.

[0053] Suitable surfactants may be selected from the compounds for improving homogenization of raw materials of adjusting foam's cellular structure, preferably from but not limited to polyoxyalkylene derivatives of siloxane, in an amount of 0.01 to 5% by weight, based on 100% by weight of B component.

[0054] The flame retardant can be an organic flame retardant or an inorganic flame retardant. The organic flame retardant is preferably but not limited to tri(2-chloroethyl)phosphate (TCEP), tri(2-chloropropyl)phosphate (TCPP), trichloropropyl phosphate (TDCPP), dimethyl methylphosphonate (DMMP), triphenyl phosphate, melamine phosphate (MMP) the mixtures thereof; the inorganic flame retardant is preferably but not limited to hydrated aluminium hydroxide, hydrated magnesium hydroxide, monoammonium phosphate, diammonium phosphate, ammonium chloride, boric acid, hydrated zinc borate (FB) or the mixture thereof.

[0055] In the polyurethane reaction system, the mole ratio of NCO groups to OH groups is preferably 70-130:100, more preferably 90-115:100, wherein the OH groups comprise all the OH groups from polyols, cross-linker, filler, blowing agent.

<u>The process for repairing polyurethane ballast bed</u>

[0056] The process provided in the present invention comprising the step of injecting the polyurethane composition in situ to the void between the sleepers and the surface of the polyurethane ballast bed such that the void is filled with a high density polyurethane rigid foam obtained from the polyurethane composition.

Because of the high density, the polyurethane rigid foam has similar or even better mechanical property and stiffness compared to sleepers, thus fixing the settled polyurethane ballast bed. Moreover, the polyurethane rigid foam and the polyurethane material in the ballast bed belong to the same kind of polymer, therefore they have better compatibility and cohesiveness.

[0057] The process of the present invention can be applied to settled polyurethane ballast bed caused by various reasons, such as geological hazard, rain washing, and heavy load of train. The settlement could be caused by the damage of the polyurethane ballast bed or ground settlement and the like.

[0058] As used herein, the void between the sleepers and the surface of the polyurethane ballast bed refers to the space between the sleeper's underside surface and the polyurethane ballast bed's surface. In the present invention, the height of the void refers to the distance from the bottom to the top of the void. The void may have different height and shape due to different cause of the settlement.

[0059] In the present invention, the height is preferably 10-100 mm. When the height is lower than 10 mm, it is not convenient to inject the polyurethane reaction system to the void, and when the height is more than 100mm, more polyurethane composition are needed to fill the void thus improving the maintenance cost.

[0060] In the present invention, the void may have irregular shape, wherein the length of the void refers to the distance of the two ends along the sleeper. The process of the present invention may be applied to any void of any length, for example 20-260 cm.

[0061] In one preferable embodiment of the present invention, the void between the sleepers and the surface of the polyurethane ballast bed is formed by lifting the track to a preset position. The void may have different height and shape according to different cause of the settlement.

[0062] The preset position can be any desirable position to a person skilled in the art, the sleeper may be lifted to the preset position by any device known to a person skilled in the art, for example, track lifting device.

[0063] In one embodiment of the present invention, the preset position is the standard height position of track, that is to say the height when the track surface is in the datum height.

[0064] Figure 1 is a schematic illustration of a process for repairing the polyurethane ballast bed in accordance with an embodiment of the present invention. As shown in figure 1, the process of repairing polyurethane ballast bed of the present

invention comprises lifting track 110 together with sleeper 120 to the standard height position of track by track lifting device 150, that is to say the track surface is in the datum height. At this moment, a void 140 is formed between the sleepers 120 and the surface of the polyurethane ballast bed 130, then the void 140 is injected with polyurethane composition, which foams and cures in situ to form a polyurethane foam to fill the void 140, thus repairing the settled polyurethane ballast bed.

[0065] In figure 1, the void 140 has a cuboid shape, which is only an example of the present invention and should not be deemed as limitation to the present invention. The void may have different shape due to the settlement of the polyurethane ballast bed.

[0066] In one embodiment of the present invention, the void 140 can be applied with a reinforcement material and then injected with the polyurethane composition, or be injected with the polyurethane composition and then applied with enforcement material before the polyurethane composition cures. When comprising reinforcement material, the obtained polyurethane foam has better strength thus is favored for supporting sleepers. In another embodiment of the present invention, the component B can be firstly mixed with reinforcement material such as sand, glass fiber, and then injected into the void by extrusion machine.

[0067] The examples of epoxy compound suitable for use in the present invention include, but not limited to alkali-free glass fabric, non-woven fabric, textile, glass fiber, carbon fiber, aramid fiber, stones, bricks, concrete blocks, metal blocks, rubber particles, plastic particles, yellow sand, glass bead and the combination thereof.

Railway system

[0068] The present invention further relates to a railway system, comprising sleepers and polyurethane ballast bed, wherein a polyurethane foam prepared from the polyurethane composition mentioned above is disposed between the sleepers and the polyurethane ballast bed to support the sleepers.

[0069] The polyurethane foam is prepared by injecting the polyurethane composition to the void 140 and cure to fill it, wherein the reinforcement material mentioned above may be comprised.

[0070] Because the polyurethane foam fills the void, the polyurethane foam has the same thickness of 10-100 mm as the void.

[0071] In addition, the polyurethane foam has a tensile strength of 2-40 Mpa, a density of 0.4-1.5 g/cm^3, a hardness of 30-90 Shore A and 40-80 shore D, and an elongation at break of 2-55 %.

Examples

[0072] The following examples are included to demonstrate preferred embodiments of the invention. It should be appreciated by those skilled in the art that the techniques disclosed in the following examples represent techniques discovered by the inventor to function well in the practice of the invention, and thus can be considered to constitute preferred modes for its practice. However, those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments which are disclosed and still obtain a similar result without departing from the spirit and scope of the invention.

[0073] The materials and devices mentioned in this invention are listed as follows:

Desmophen 4050 E, the first polyether polyol, EDA as initiator, OH number 620, functionality 4.0, supplied by Bayer materialscience Ltd;

Desmophen 4051 B, the first polyether polyol, EDA as initiator, OH number 470, functionality 4.0, supplied by Bayer materialscience Ltd;

GR 403, the first polyether polyol, EDA as initiator, OH number 770, functionality 4.0, supplied by Shanghai Gaoqiao PU company;

GR 405, the first polyether polyol, EDA as initiator, OH number 450, functionality 4.0, supplied by Shanghai Gaoqiao PU company;

Arcol 1026, second polyether polyol, PG as initiator, OH number 28, functionality 2.0 supplied by Bayer materialscience Ltd;

Arcol 1021, second polyether polyol, PG as initiator, OH number 56, functionality 2.0 supplied by Bayer materialscience Ltd;

Arcol 3553, second polyether polyol, glycerin as initiator, OH number 35, functionality 3.0 supplied by Bayer materialscience Ltd;

Arcol 1362, second polyether polyol, glycerin as initiator, OH number 28, functionality 3.0 supplied by Bayer materialscience Ltd;

GE 220, second polyether polyol, PG as initiator, OH number 56, functionality 2.0 supplied by Shanghai Gaoqiao PU company;

GR 635, third polyether polyol, sorbitol/glycerin mixture as initiator, OH number 500, functionality 4.5, supplied by Shanghai Gaoqiao PU company;

Arcol 3601, third polyether polyol, sorbitol/glycerin mixture as initiator, OH number 360, functionality 4.2, supplied by Bayer materialscience Ltd;

Arcol 3607, third polyether polyol, sorbitol/glycerin mixture as initiator, OH number 450, functionality 4.7, supplied by Bayer materialscience Ltd;

Desmophen 21AP27, third polyether polyol, sorbitol/EG mixture as initiator, OH number 440, functionality 2.8, supplied by Bayer materialscience Ltd;

GE 303, third polyether polyol, glycerin as initiator, OH number 480, functionality 3.0 supplied by Shanghai Gaoqiao PU company;

Stepanpoly PS-1922, PTA polyester polyol, OH number 190, functionality 2.0, supplied by Stepan;

Tego Stab B 8715, stabilizer, supplied by Evonik;

DEG, diethylene glycol, chain extender, common chemical product;

DPG, dipropylene glycol, chain extender, common chemical product;

DBTDL, Dibutyltindilaurate, catalyst, supplied by Air Products

KAC/DEG solution, catalyst, common chemical product;

Desmodur 44 V20L, PMDI, NCO 31.5%, supplied by Bayer materialscience Ltd;

Desmodur 44 P90, MDI prepolymer, NCO28.1%, supplied by Bayer materialscience Ltd;

Desmodur 1511L, PMDI, NCO 31.5%, supplied by Bayer materialscience Ltd;

H-XP3 type spray machine, with mix head: supplied by GRACO company;

YQ-245 hydraulic rail lifter, YUFENG hydraulic machinery company LTD;

CG-600-1-1, Caulking gun, supplied by Naishangjiong company.

Example 1

[0074] The rails, together with the fasteners and sleepers were lifted up by YQ-245 hydraulic lifting device to the standard height position of the track, thus a void with a height of about 25 mm was formed between sleeper and polyurethane ballast bed. The void was first filled with small gravel ballast. Polyether polyols were mixed according to table 1 at room temperature. The mixed polyols and isocyanate were injected to the void within 60s by GC-600-1-1 caulking gun. After 30 minutes the polyurethane composition cured to form a polyurethane foam filling the void between the sleepers and the polyurethane ballast bed.

Table 1: the polyurethane composition and the Physical and mechanical properties thereof

Item		unit	Example 1	standard
Polyol system	Desmophen 4050E	pbw	32.00	Material temperature 25 °C
	Desmophen 21AP27	pbw	32.00	Material temperature 25 °C
	Arcol 1362	pbw	35.00	Material temperature 25 °C
	B8715(Evonik)	pbw	1.00	Material temperature 25 °C
Desmodur 44V20L		pbw	100	Material temperature 25 °C
Physical and mechanical properties				
Density		kg/m^3	1180	DIN EN ISO 845
Hardness		Shore D	80	DIN 53505
Flexural strength		MPa	75	DIN EN ISO 178
Flexural modulus		MPa	1600	DIN EN ISO 178
Impact strength		KJ/m^2	40	DIN EN ISO 179
Compress strength		N/mm^2	65	DIN 53421
Tensile strength		MPa	45	DIN EN ISO 527-2
Elongation		%	10	DIN EN ISO 527
Tensile modulus		MPa	1650	DIN EN ISO 527-2

[0075] The polyurethane foam of the present example is prepared by the way of onsite casting and in situ reaction, thus has a wide application for the cases wherein the sleepers has an irregular bottom surface or the polyurethane ballast bed has an irregular surface.

Example 2-3

[0076] The rails, together with the fasteners and sleepers were lifted up by YQ-245 hydraulic lifting device to the standard height position of the track, thus a void with a height of about 25 mm was formed between sleepers and the polyurethane ballast bed. The polyurethane compositions according to table 2 were injected to the void within 30s by conventional H-XP3 high pressure foam machine. After 30 minutes the polyurethane composition cured to form a polyurethane foam mat filling the void between the sleepers and the polyurethane ballast bed.

Table 2: the polyurethane composition and the physical and mechanical properties thereof

Item	Unit	Example 2	Example 3	standard
Arcol 3553	pbw	69.60	69.60	Material temperature 25 °C
Desmophen 3601	pbw	10.00	10.0	Material temperature 25 °C
Desmophen 4051B	pbw	20.00	20.0	Material temperature 25 °C
DBTDL	pbw	0.005-0.02	0.005-0.02	Material temperature 25 °C
Acetate K / diethylene glycol solution	pbw	0.40	0.40	Material temperature 25 °C
Glass fiber	pbw	0	35	Material temperature 25 °C
Desmodur 44P90	pbw	100	100	Material temperature 25 °C
physical and mechanical properties				
Density	kg/m^3	1.18	1.35	DIN EN ISO 845
Hardness	Shore D	76	76	DIN 53505
Flexural strength	MPa	38	70	DIN EN ISO 178
Flexural modulus	MPa	790	2500	DIN EN ISO 178
Impact strength	KJ/m^2	65	29	DIN EN ISO 179
Tensile strength	Mpa	32	45	DIN EN ISO 527-2
Elongation	%	12	6	DIN EN ISO 527
Tensile modulus	Mpa	780	2480	DIN EN ISO 527-2

[0077] The polyurethane composition in example 3 comprising glass fiber has better physical properties, for instance tensile strength and elongation.

Example 4

[0078] The rails, together with the fasteners and sleepers were lifted up by YQ-245 hydraulic lifting device to the standard height position of the track, thus a void with a height of about 50 mm was formed between sleeper and polyurethane ballast bed. The void was first filled with continuous Z-type pads which were prepared by folding glass fiber cloth and kraft paper. The component B was first mixed according to table 3 under room temperature, and then injected to the void with isocyanates at a ratio of 1:1 within 30s by conventional H-XP3 high pressure foam machine. After 30 minutes the polyurethane composition is cured to form a polyurethane foam mat filling the void between the sleepers and the polyurethane ballast bed.

Table 3: the polyurethane composition and the physical and mechanical properties thereof

Item	Unit	Example 4	standard
GR 403	pbw	35	Material temperature 25 °C
GR 405	pbw	20	Material temperature 25 °C
GE 220	pbw	30	Material temperature 25 °C
GE 303	pbw	15	Material temperature 25 °C
Desmodur PU 1511 L	pbw	100	Material temperature 25 °C
Physical and mechanical properties			
Density	kg/m^3	1150	DIN EN ISO 845
Hardness	Shore D	75	DIN 53505
Tensile strength	MPa	52	DIN EN ISO 527-2
Elongation	%	4	DIN EN ISO 527
Flexural strength	MPa	55	DIN EN ISO 178
Flexural modulus	MPa	2200	DIN EN ISO 178
Impact strength	KJ/m^2	45	DIN EN ISO 179
Compressive strength	N/mm^2	68	DIN 53421

[0079] The polyurethane foam mat of the present example is prepared by the way of onsite casting and in situ reaction, thus has a wide application for the cases wherein the sleepers has an irregular bottom surface or the polyurethane ballast bed has an irregular surface. Moreover, the polyurethane composition has a fast curing speed which is basically unaffected by environment temperature, thus well suited for fast repairing and repairing work at cold or high elevation area.

CLAIMS

1. A polyurethane composition for repairing polyurethane ballast bed, comprising:

(a) one or more polyisocyanate;

(b) a polyether polyol mixture comprising:

(b1) a first polyether polyol selected from amine initiated polyether polyols having a functionality of 2-6 and a hydroxyl number of 10-1200 mg KOH/g;

(b2) a second polyether polyol selected from polyol initiated polyether polyols having a functionality of 2-3 and a hydroxyl number of 12-120 mg KOH/g;

(b3) a third polyether polyol selected from polyol initiated polyether polyols having a functionality of 3-8 and a hydroxyl number of 150-1200 mg KOH/g;

Wherein the first polyether polyol has an amount of 10-60 wt. %, the second polyether polyol has an amount of 1-70 wt. %; the third polyether polyol has an amount of 10-70 wt. %, based on 100 % by weight of the polyether polyol mixture.

2. The polyurethane composition according to claim 1, wherein the first polyether polyol has a functionality of 4-6 and a hydroxyl number of 300-1000 mg KOH/g.

3. The polyurethane composition according to claim 2, wherein the first polyether polyol has a functionality of 4 and a hydroxyl number of 400-800 mg KOH/g.

4. The polyurethane composition according to any one of claims 1-3, wherein the first polyether polyol has an amount of 30-60 wt.%, based on the 100 % by weight of the polyether polyol mixture.

5. The polyurethane composition according to claim 1, wherein the second polyether polyol has a functionality of 2-3 and a hydroxyl number of 25-60 mg KOH/g.

6. The polyurethane composition according to claim 1, wherein the second polyether polyol has an amount of 10-30 wt.%, based on 100 % by weight of the polyether polyol mixture.

7. The polyurethane composition according to claim 1, wherein the third polyether polyol has a functionality of 3-6 and a hydroxyl number of 150-900 mgKOH/g.

8. The polyurethane composition according to claim 1, wherein the third polyether polyol has a functionality of 3-5 and a hydroxyl number of 250-700 mgKOH/g.

9. The polyurethane composition according to claim 1, wherein the third polyether polyol has an amount of 30-50 wt.%, based on 100 % by weight of the polyether polyol mixture.

10. The polyurethane composition according to claim 1, wherein the polyisocyanate is the one or more selected from the group consisting of diphenylmethane diisocyanate, toluene diisocynate or the combination thereof.

11. A process for repairing settled polyurethane ballast bed, wherein the sleepers for supporting the track are disposed on the ballast bed, the process comprising the step of injecting the polyurethane composition according to any one of claims 1-10 to the void between the sleepers and the surface of the polyurethane ballast bed such that the polyurethane composition cures to fill the void.

12. The process according to claim 11, wherein the void between the sleepers and the surface of the polyurethane ballast bed is formed by lifting the track to a preset position.

13. The process according to claim 11 or 12, wherein the void between the sleepers and the surface of the polyurethane ballast bed has a height of about 10-100 mm.

14. The process according to claim 11, wherein the process further comprises the step of applying reinforcement material.

15. The process according to claim 14, wherein the reinforcement material is the one or more selected from the group consisting of alkali-free glass fabric, non-woven fabric, textile, glass fiber, carbon fiber, aramid fiber, stones, bricks, concrete blocks, metal blocks, rubber particles, plastic particles, yellow sand, glass bead and the combination thereof.

16. A railway system, comprising sleepers and polyurethane ballast bed, wherein a polyurethane foam prepared from the polyurethane composition according to any one of claims 1-10 is disposed between the sleepers and the polyurethane ballast bed to support the sleepers.

17. The railway system according to claim 16, wherein the polyurethane foam has a thickness of 10-100 mm.

18. The railway system according to claim 16, wherein the polyurethane foam has a tensile strength of 2-40 Mpa, and a hardness of 30-90 Shore A and 40-80 shore D.

19. The railway system according to claim 16, wherein the polyurethane foam has a density of 1.5 g/cm^3 and an elongation at break of 2-55 %.

Drawings

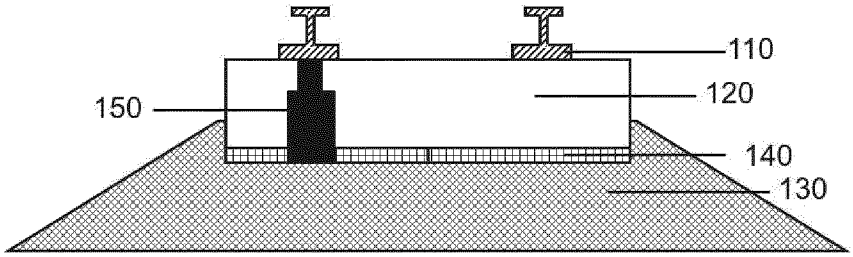


Figure 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/069894

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G18/48 C08G18/50 C08G18/66 C08G18/76 C08G18/32
E01B27/00
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 E01B

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

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2011/074642 A1 (ASAHI GLASS CO LTD [JP]; SHIMIZU KATSUHIKO [JP]; WADA HIROSHI [JP]; TO) 23 June 2011 (2011-06-23)	1-10
Y	claims 1-12 examples 1-16	11-19

Y	US 2004/176490 A1 (GIORGINI ALBERT M [US] ET AL) 9 September 2004 (2004-09-09) tables I-II claims 1-23 paragraphs [0039] - [0041]	11-19

Y	WO 2012/044338 A1 (DOW GLOBAL TECHNOLOGIES LLC [US]; LAZRAQ ISSAM [NL]; STEGT HELMUT [DE]) 5 April 2012 (2012-04-05) examples 1-4	11-19

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
1 November 2013	07/11/2013

Name and mailing address of the ISA/	Authorized officer
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Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/069894

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2011/131621 A1 (BAYER MATERIALSCIENCE AG [DE]; ZHANG CHENXI [SG]; SUN GANG [CN]; SHEN) 27 October 2011 (2011-10-27) claims 1-10 examples 1-4 -----	1-19

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2013/069894

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2011074642 A1	23-06-2011	CA 2784403 A1	23-06-2011
		CN 102666628 A	12-09-2012
		EP 2514780 A1	24-10-2012
		KR 20120107960 A	04-10-2012
		US 2012251727 A1	04-10-2012
		WO 2011074642 A1	23-06-2011
US 2004176490 A1	09-09-2004	CA 2420777 A1	04-09-2004
		MX PA03001931 A	29-10-2004
		US 2004176490 A1	09-09-2004
		US 2006293488 A1	28-12-2006
WO 2012044338 A1	05-04-2012	CN 103221445 A	24-07-2013
		EP 2621987 A1	07-08-2013
		US 2013184368 A1	18-07-2013
		WO 2012044338 A1	05-04-2012
WO 2011131621 A1	27-10-2011	AU 2011244434 A1	08-11-2012
		EP 2561138 A1	27-02-2013
		JP 2013525636 A	20-06-2013
		US 2013140373 A1	06-06-2013
		WO 2011131621 A1	27-10-2011