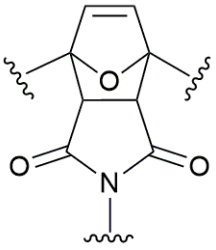
CLAIMS

1. A method of crosslinking a polyhydroxyurethane (PHU) polymer having a plurality of diene moieties in the backbone, the method comprising:

reacting a crosslinking agent having two or more dienophile moieties with the PHU polymer backbone to form crosslinks between the diene moieties via a plurality of diene-dienophile adducts,

wherein at least a part of the diene-dienophile adduct comprises structure (I):



Structure (I).

2. The method according to claim 1, wherein the crosslinking occurs below a threshold temperature beyond which crosslinks are removed from the PHU polymer.

3. The method according to any one of claims 1 to 2, wherein the crosslinking is carried out at ambient room temperature or above.

4. The method according to any one of claims 1 to 3, wherein the diene moiety comprises a furan moiety.

5. The method according to any one of claims 1 to 4, wherein the dienophile moiety comprises a maleimide moiety.

6. The method according to any one of claims 1 to 5, wherein the crosslinking agent is a bismaleimide.

7. The method according to claim 6, wherein the bismaleimide is selected from the group consisting of 1,1’-(Methylenedi-4,1-phenylene)bismaleimide (BM1), N,N’-hexamethylenebismaleimide, (BM2), N,N’-(1,4-Phenylene)dimaleimide (BM3) and N,N’-pentamethylenebismaleimide (BM4).

8. The method according to any one of claims 1 to 7, wherein the PHU polymer and the crosslinking agent are reacted in a molar ratio of 1 : 0.05 – 1.

9. The method according to any one of claims 1 to 8, further comprising, reacting at least one biscarbonate with at least one amine containing compound to form the PHU polymer, prior to reacting the PHU polymer with the crosslinking agent,

wherein at least one of the biscarbonate or amine containing compound comprises a diene moiety.

10. The method according to claim 9, wherein the biscarbonate is selected from the group consisting of sebacate bis-carbonate (SBC), terephthalic bis-carbonate (TBC), benzene bis-carbonate (BBC), methyl bis-carbonate (MBC), succinic bis-carbonate (SuBC), bis((2-oxo-1,3-dioxolan-4-yl)methyl)furan-2,5-dicarboxylate (FBC1), 4,4'-(((furan-2,5-diylbis(methylene))bis(oxy))bis(methylene))bis(1,3-dioxolan-2-one) (FBC2), bis((2-oxo-1,3-dioxolan-4-yl)methyl)pyridine-2,5-dicarboxylate (PBC), bis((2-oxo-1,3-dioxolan-4-yl)methyl)pyridine-2,6-dicarboxylate (PBC-2) and 4,4'-(((tetrahydrofuran-3,4-diyl)bis(oxy))bis(methylene))bis(1,3-dioxolan-2-one) (HFBC), and the amine containing compound is selected from the group consisting of

furan bis-amine (FBA), xylene diamine (XDA), diaminopentane (DAP) and hexamethylenediamine (HDA).

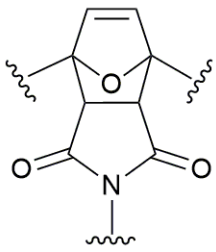
11. The method according to any one of claims 9 to 10, wherein the biscarbonate is prepared from a bio-based source.

12. The method according to any one of claims 9 to 10, wherein the amine containing compound is prepared from a bio-based source.

13. The method according to any one of claims 1 to 12, further comprising, functionalizing the PHU polymer with one or more substituents selected from the group consisting of alkyl, sulfate, sulfonate, phosphate, carboxylate, sulfobetaine, phosphobetaine, cinnamate, fatty acid, amino acid, lactic acid, polylactic acid, caprolactone, polycaprolactone, polysiloxane and combinations thereof to form a functionalized PHU polymer, prior to reacting said PHU polymer with the crosslinking agent.

14. A crosslinked polyhydroxyurethane (PHU) polymer obtained from the method of any one of claims 1 to 13, the crosslinked polymer comprising a plurality of diene-dienophile adducts,

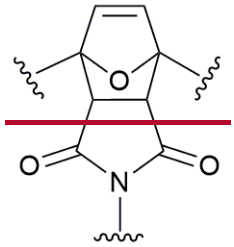
wherein at least a part of the diene-dienophile adduct comprises structure (I):



Structure (I).

15. The crosslinked polymer according to claim 14, wherein the diene-dienophile adduct ~~comprises a ring structure~~is formed from a Diels-Alder reaction between the diene moiety and the dienophile moiety.

~~16. The crosslinked polymer according to any one of claims 14 to 15, wherein at least a part of the Diels-Alder adduct comprises structure (I):~~



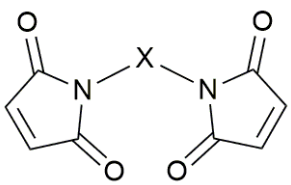
~~Structure (I)~~

~~17.~~16. The crosslinked polymer according to any one of claims 14 to ~~16~~15, wherein the crosslinked polymer is devoid of an isocyanate group.

~~18.~~17. The crosslinked polymer according to any one of claims 14 to ~~17~~16, wherein the diene moiety comprises furan.

~~19.~~18. The crosslinked polymer according to any one of claims 14 to ~~18~~17, wherein the dienophile moiety comprises maleimide.

~~20.~~19. The crosslinked polymer according to any one of claims 14 to ~~19~~18, wherein the ~~maleimide~~crosslinking agent is a bismaleimide represented by general formula (I):



(I)

wherein X is a single bond, C_1-C_{14} alkylene, polyethyleneglycol (PEG) or segments thereof, polypropylene glycol (PPG) or segments thereof, phenylene, methylenebis(phenylene), sulfonylbis(phenylene), oxybis(phenylene) and combinations thereof.

~~21.~~20. The crosslinked polymer according to claim ~~20~~19, wherein the ~~maleimide is a~~ bismaleimide is selected from the group consisting of 1,1'-(Methylenedi-4,1-phenylene)bismaleimide (BM1), N,N'-hexamethylenebismaleimide, (BM2),N,N'-(1,4-Phenylene)dimaleimide (BM3) and N,N'-pentamethylenebismaleimide (BM4).

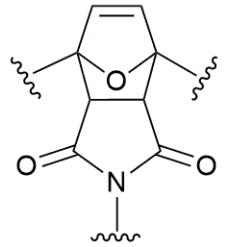
~~22.~~21. The crosslinked polymer according to any one of claims 14 to ~~21~~20, wherein the crosslinks are removable at a temperature of more than 50°C.

~~23.~~22. The crosslinked polymer according to any one of claims 14 to ~~22~~21, wherein the crosslinked polymer has one or more of the following properties: easily recyclable, self-healing, thermo-healing and shape memory.

~~24.~~23. A method of removing the crosslinks of a crosslinked polyhydroxyurethane (PHU) polymer comprising a plurality of diene-dienophile adducts, the method comprising:

heating the crosslinked PHU polymer at a temperature of from more than 50°C to remove the crosslinks,

wherein at least a part of the diene-dienophile adduct comprises structure (I):



Structure (I).

25.24. A coated substrate comprising:

a layer of crosslinked polyhydroxyurethane (PHU) polymer according to any one of claims 14 to 2322 disposed over a surface of the substrate.

26.25. The coated substrate according to claim 2524, wherein the substrate is selected from the group consisting of wood, glass, metal, plastic and fabric and combinations thereof.