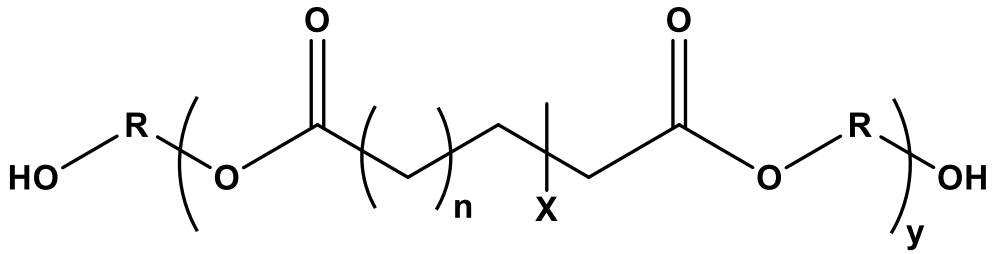
[0010a] In one aspect of the present disclosure, there is provided a thermoplastic polyurethane elastomer composition comprising the reaction product of

(a) a composition (NO_2-PED) comprising

(i) at least one nitro-substituted polyester diol, wherein such polyester diol is substituted with the nitro group between the two carboxy groups of the polyester diol, and

(ii) at least one polyester diol that is not substituted by a nitro group, wherein the nitro-substituted polyester diol has the formula:



wherein n is 0-14, y is 1-100, X=H or NO_2, and R is alkylenyl, alkylenyl with one or more CH_2 groups substituted by -O-, cycloalkylenyl, or arylenyl, wherein at least one X is NO_2

(b) at least one polyisocyanate, and

(c) at least one chain extender.

[0010b] In another aspect of the present disclosure, there is provided a method for making the composition disclosed herein, comprising reacting:

(a) at least one nitro-substituted polyester diol (NO_2-PED),

(b) at least one polyisocyanate and

(c) at least one chain extender.

[0010c] In a further aspect of the present disclosure, there is provided a method of making a polyurethane foam, the method comprising reacting:

(a) a polyester comprising at least one nitro-substituted polyester diol,

(b) at least one isocyanate,

(c) at least one chain extender,

(d) at least one flame retardant,

(e) at least one surfactant,

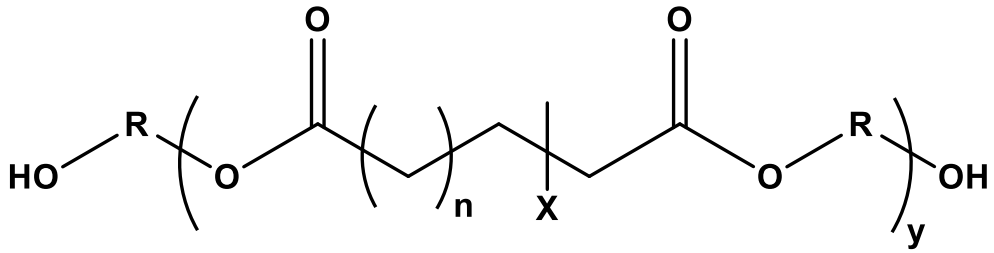
WHAT IS CLAIMED IS:

1. A thermoplastic polyurethane elastomer composition comprising the reaction product of

(a) a composition (NO_2-PED) comprising

(i) at least one nitro-substituted polyester diol, wherein such polyester diol is substituted with the nitro group between the two carboxy groups of the polyester diol, and

(ii) at least one polyester diol that is not substituted by a nitro group, wherein the nitro-substituted polyester diol has the formula:



wherein n is 0-14, y is 1-100, X=H or NO_2, and R is alkylenyl, alkylenyl with one or more CH_2 groups substituted by -O-, cycloalkylenyl, or arylenyl, wherein at least one X is NO_2

(b) at least one polyisocyanate, and

(c) at least one chain extender.

2. The composition of claim 1, wherein R is alkylenyl.

3. The composition of claim 1 or 2, wherein R is ethylenyl, propylenyl, isopropylenyl, butylenyl, pentylenyl, hexylenyl, heptylenyl, or octylenyl.

4. The composition of any one of claims 1-3, wherein R is alkylenyl, wherein one or more CH_2 groups are substituted by –O-.

5. The composition of any one of claims 1-4, wherein R is $–(CH_2)_o-O-(CH_2)_o-$, $-CH(CH_3)-(CH_2)_o-O-(CH_2)_o-CH_2-$, or $-CH(CH_3)-(CH_2)_o-O-(CH_2)_o-CH(CH_3)-$, wherein o is 1-4.

6. The composition of claim 1, wherein R is arylenyl.

7. The composition of any one of claims 1-6, in which the NO_2-PED before reaction has a molecular weight of 400-10,000 g/mol.

8. The composition of any one of claims 1-7, wherein the chain extender is a dihydroxyalkane or dihydroxycycloalkane.

9. The composition of any one of claims 1-8, wherein the chain extender is ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, 1,10-decanediol, neo-pentyl glycol, 1,4-cyclohexanedimethanol, 1,4-dihydroxycyclohexane, or mixtures thereof.

10. The composition of any one of claims 1-7, wherein the chain extender is an alkylene, aralkylene, or cycloalkylene diamine.

11. The composition of any one of claims 1-7 or 10, wherein the chain extender is ethylene diamine, hexamethylene diamine, 1,4-cyclohexanylene diamine, or mixtures thereof.

12. The composition of any one of claims 1-7, wherein the chain extender is an aromatic diamine.

13. The composition of any one of claims 1-7 or 12, wherein the aromatic diamine is benzidine, toluene diamine, diaminodiphenyl methane, phenylene diamine, or mixtures thereof.

14. The composition of any one of claims 1-7, wherein the chain extender is hydrazine.

15. The composition of any one of claims 1-7, wherein the chain extender is an amino alcohol.

16. The composition of any one of claims 1-7 or 15, wherein the chain extender is ethanolamine, N-methylethanolamine, N-butylethanolamine, N-oleoylethanolamine, N-cyclohexylisopropanolamine, or mixtures thereof.

17. The composition of any one of claims 1-7, wherein the chain extender is a substituted aromatic diamine.

18. The composition of any one of claims 1-7 or 17, wherein the chain extender is 4,4'-methylene-bis(o-chloroaniline), 4,4'-methylenebis(3-chloro-2,6-diethylaniline), or mixtures thereof.

19. The composition of any one of claims 1-18, wherein the thermoplastic polyurethane elastomer composition further comprises at least one crosslinking agent.

20. The composition of claim 19, wherein the at least one crosslinking agent is glycerine, trimethylolpropane, diethanolamine, triethanolamine, or mixtures thereof.

21. The composition of any one of claims 1-20, wherein a ratio of polyisocyanate to active hydrogen containing group (the NCO index) is from 0.9-1.5.

22. The composition of any one of claims 1-21, wherein the at least one polyisocyanate is 4,4'-diisocyanatodiphenylmethane (4,4'-MDI), 2,4'-diisocyanato diphenylmethane (2,4'-MDI), p-phenylene diisocyanate, 1,3-bis(isocyanatomethyl)cyclohexane, 1,4-diisocyanato cyclohexane, hexamethylene diisocyanate, isophorone diisocyanate, 1,5-naphthalene diisocyanate, 3,3'-dimethyl-4,4'-biphenyl diisocyanate, 4,4'-diisocyanato-dicyclohexylmethane, 2,6-toluene diisocyanate, 2,4-toluene diisocyanate, or mixtures thereof.

23. The composition of any one of claims 1-22, further comprising at least one additive comprising:

(a) a light stabilizer or a UV stabilizer;

(b) an inorganic filler or an organic filler;

(c) a silicate mineral, metal oxide, metal salt, clay, metal silicate, glass fiber, natural fibrous material, or a synthetic fibrous mineral;

(d) carbon black, fullerene, carbon nanotubes, biochar, melamine colophony, cellulose fibers, polyamide fibers, polyacrylonitrile fibers, polyurethane fibers, polyester fibers based on aromatic and/or aliphatic dicarboxylic acid esters, or carbon fibers; and

(e) an organic phosphate, metal polyphosphate, metal oxide, metal salt, or a cyanuric acid derivative;

wherein the additives are present in 0.5-30 percent by weight of the composition.

24. The composition of any one of claims 1-23, further comprising at least one flame retardant that is an organic phosphate, metal polyphosphate, metal oxide, metal salt, cyanuric acid derivative, or mixtures thereof; wherein the at least one flame retardant is present in 500 to 4000 ppm of the composition.

25. The composition of any one of claims 1-24, further comprising a foaming agent that is water, pentane, cyclopentane, or a hydrofluorocarbon, or mixtures thereof.

26. The composition of any one of claims 1-25, wherein the at least one nitro-substituted polyester diol comprises at least one C8-C20 dicarboxylic acid substituted with a single nitro group, and at least one polyol.

27. The composition of claim 26, wherein the at least one polyol is a C_{1-8} diol.

28. The composition of any one of claims 1-27, which comprises 20-80% by weight of the nitro-substituted polyester diol (NO_2-PED).

29. The thermoplastic polyurethane elastomer composition of any one of claims 1-28, in the form of a foam.

30. The thermoplastic polyurethane elastomer composition of any one of claims 1-29, in the form of a foam containing:

(a) a polyester comprising at least one nitro-substituted polyester diol,

(b) at least one isocyanate,

(c) at least one chain extender,

(d) at least one flame retardant,

(e) at least one surfactant,

(f) at least one foaming agent, and

(g) at least one urethane catalyst.

31. A method for making the composition of any one of claims 1-30, comprising reacting:

(a) at least one nitro-substituted polyester diol (NO_2-PED),

(b) at least one polyisocyanate and

(c) at least one chain extender.

32. The method of claim 31, wherein the reacting is conducted at a temperature of from 25 to 120 °C.

33. The method of claim 31 or 32, comprising the steps of:

- blending (a) and (c) in a reaction vessel; and
- adding (b) to the vessel while stirring.

34. The method of claim 31 or 32, comprising the steps of:

- reacting (a) and (b) at temperatures up to 80°C;
- adding a catalyst and (c) while stirring, and allowing to react at temperatures up to 120°C.

35. The method of any one of claims 31 to 34, wherein:

- the NO_2-PED is 20 to 80 wt.% of the thermoplastic polyurethane;
- the polyisocyanate is 20 to 80 wt.% of the thermoplastic polyurethane; or
- the chain extender is 1 to 20 wt.% of the thermoplastic polyurethane.

36. A method of making a polyurethane foam, the method comprising reacting:

(a) a polyester comprising at least one nitro-substituted polyester diol,

(b) at least one isocyanate,

(c) at least one chain extender,

(d) at least one flame retardant,

(e) at least one surfactant,

(f) at least one foaming agent, and

(g) at least one urethane catalyst;

to form a foam having a continuous phase comprising a thermoplastic polyurethane elastomer.

37. The method of claim 36, further comprising reacting at least one polyester diol not substituted with a nitro group.

38. The method of claim 36 or 37, wherein the polyester diol and nitro-polyester diol are dicarboxylic acid esters of:

a. oxalic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid,azelaic acid, C_{10}-dicarboxylic acid, C_{11}-dicarboxylic acid, C_{12}-dicarboxylic acid, C_{13}-dicarboxylic acid, C_{14}-dicarboxylic acid and C_{15}-dicarboxylic acid, and

b. at least one C_8-C_{20} dicarboxylic acid substituted with a single nitro group; and at least one diol.

39. The method of any one of claims 36 to 38, wherein the at least one diol is a C_{1-8} diol.

40. Use of the composition of any one of claims 1-30, for preparing molded articles such as soles for footwear, hard solid plastics such as for electronic instrument bezels and structural parts, flexible plastics such as straps and bands, and for seals, gaskets, durable elastomeric wheels and tires, automotive suspension bushings, and electrical insulating parts.

41. Use of the composition of any one of claims 1-30, for 3D printing when the compositions are extruded into filament.

42. Use of the composition of any one of claims 1-30, wherein the compositions is pelletized and expanded to yield expanded TPU foams for footwear applications.