equal or better performance than their traditional petroleum-based alternatives at a comparable price point.

[0005] U.S. Patent No. 5,844,165 discloses nitromalonate polyesters that are useful in high energy propellants. According to this '165 patent, preferred nitromalonate polyesters contain R^1 and R^2 groups that are both $–CH_2ONO_2$. Thus, the preferred nitromalonates described by this '165 patent are substituted by two nitro-methane groups between the two carboxy groups of the malonate, providing an energetic composition.

[0006] U.S. Patent No. 3,745,076 discloses the reaction product of 4,4-dinitropimelic acid and diethylene glycol that results in a polester polyol containing hydroxy groups that can be reacted with polyisocyanates. According to this '076 patent, when the nitro is the substituent group, there should preferably be at least two nitro groups present on the substituted component. The multiple nitro groups are preferred, as it is an object of this '076 patent to produce a binder having a higher total energy content.

SUMMARY

[0007] The following examples and aspects thereof are described and illustrated in conjunction with systems, compositions, methods, and articles of manufacture which are meant to be exemplary and illustrative, not limiting in scope.

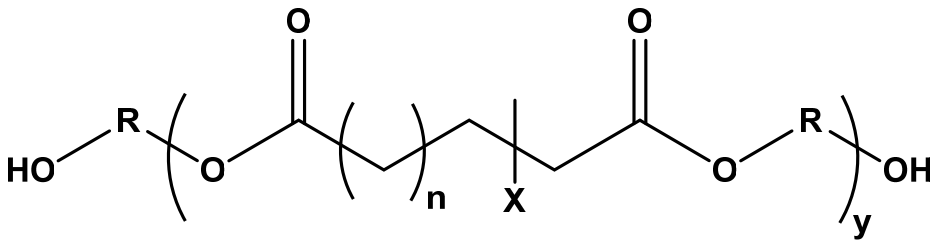
[0008] Post-consumer polyethylene waste provides an abundant source of raw material for making new chemicals. Nitro-functionalized diacids are the product of chemically recycled polyethylene via Accelerated Thermal Oxidative Decomposition (ATOD™). These diacids can be used to synthesize nitro-functionalized polyester diols which are a major building block for thermoplastic polyurethanes. These nitro-functionalized polyester diols are the first polyols synthesized from monomers derived from chemically recycled post-consumer polyethylene.

[0009] It would be desirable to provide a TPU elastomer from a polyester diol that is economical, is made from recycled content, and exhibits excellent mechanical properties.

[0010] It is, accordingly, an object of the present disclosure to overcome deficiencies in the prior art described above. It is another object to provide polyester based TPU elastomers with increased hardness and tensile strength while maintaining elasticity.

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

(a) a composition comprising at least one nitro-substituted polyester diol (NO_2-PED), wherein the NO_2-PED is substituted with the nitro group between the two carboxy groups of the NO_2-PED, and at least one polyester diol that is not substituted by a nitro group, wherein the NO_2-PED 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,

(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.

[0010d] In another aspect of the present disclosure, there is provided a use of the composition disclosed herein, 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.

[0010e] In a further aspect of the present disclosure, there is provided a use of the composition disclosed herein, for 3D printing when the compositions are extruded into filament.

[0010f] In another aspect of the present disclosure, there is provided a use of the composition disclosed herein, wherein the compositions is pelletized and expanded to yield expanded TPU foams for footwear applications.

[0011] This present disclosure provides a TPU elastomer which is a polymer of (1) at least one high equivalent weight polyester diol containing nitro functionality on the backbone

derived from mixtures of dicarboxylic acids and nitro-dicarboxylic acids as well as a polyesterdiol not containing any nitro groups, (2) at least one chain extender and (3) at least one diisocyanate. The presence of polyesterdiol not containing any nitro groups provides a non-energenic TPU useful for consumer goods.

[0012] In another example, provided is a TPU elastomer which is a polymer of (1) 20-80% by weight of nitro-functionalized polyester diol (NO_2-PED) made from a mixture of dicarboxylic acids, nitro-dicarboxylic acids, and 1,4-butanediol, or a mixture thereof with at least one chain extender mixture, and (3) at least one polyisocyanate.

[0013] The present disclosure also comprising a NO_2-PED synthesized from chemically recycled monomers derived from the decomposition of post-consumer polyethylene. The resulting TPU's provide a sustainable alternative to bio- or petrochemical-based TPU's.

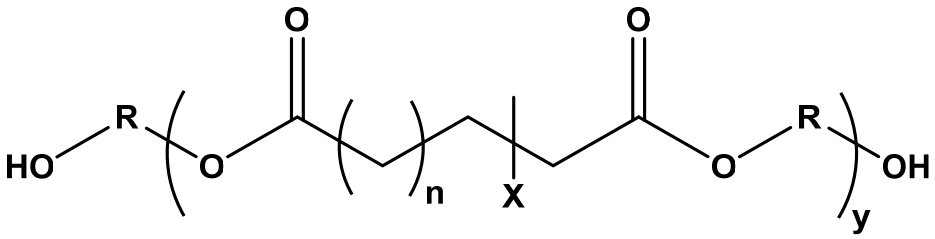
[0014] We found that the unique nitro functionality on the high equivalent weight polyester diol component contributed to higher glass transition temperatures, higher tensile strength, and greater Shore A hardness.

[0015] Provided is a thermoplastic polyurethane elastomer composition comprising the reaction products of:

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

at least one polyisocyanate, and further comprising the reaction product with at least one chain extender.

[0016] In some examples, NO_2-PED has the formula:



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

[0017] In some examples, R is alkylenyl. In some examples, R is ethylenyl, propylenyl, isopropylenyl, butylenyl, pentylenyl, hexylenyl, heptylenyl, or octylenyl.

[0018] In some examples, R is alkylenyl, wherein one or more CH_2 groups are substituted by –O-.

[0019] In some examples, R is $–(CH_2)_o$-O-$(CH_2)_o$-, CH_3-O-$(CH_2)_o$-O-$(CH_2)_o$- CH_3, $(CH_3CH(OH)CH_2)_2O$, wherein o is 2-4**.**

[0020] In some examples, R is arylenyl or aralkylenyl.

[0021] In some examples, the NO_2-PED before reaction has a molecular weight of 400-10,000 g/mol.

[0022] In some examples, the chain extender is a dihydroxyalkane or dihydroxycycloalkane. In some examples, 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.

[0023] In some examples, the chain extender is an alkylene or aralkylene diamine. In some examples, the chain extender is ethylene diamine, hexamethylene diamine, 1,4-cyclohexanylene diamine, or mixtures thereof. In some examples, the chain extender is an aromatic diamine. In some examples, the aromatic diamine is benzidine, dihydroxymethoxy hydroquinone, toluene diamine, diaminodiphenyl methane, phenylene diamine, or mixtures thereof.

[0024] In some examples, the chain extender is hydrazine.

[0025] In some examples, the chain extender is an amino alcohol. In some examples, the chain extender is ethanolamine, N-methylethanolamine, N-butylethanolamine, N-oleoylethanolamine, N-cyclohexylisopropanolamine, or mixtures thereof.

[0026] In some examples, the chain extender is a substituted aromatic diamine. In some examples, the chain extender is 4,4'-methylene-bis(o-chloroaniline), 4,4'-methylenebis(3-chloro-2,6-diethylaniline), or mixtures thereof.

[0027] In some examples, the thermoplastic polyurethane elastomer composition further comprises at least one crosslinking agent. In some examples, the crosslinking agent is glycerine, trimethylolpropane, diethanolamine, triethanolamine, or mixtures thereof.

[0028] In some examples, the ratio of polyisocyanate to active hydrogen containing group (the NCO index) is from 0.9-1.5.

[0029] In some examples, the isocyanate 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. In some examples, the isocyanate is 4,4'-MDI or 2,4'-MDI.

[0030] In some examples, the composition comprises one or more additives. In some examples, the one or more additives comprise at least one light stabilizer, UV stabilizer, or mixtures thereof. In some examples, the one or more additives are an inorganic filler, organic filler, or mixtures thereof. In some examples, the one or more additives are at least one inorganic filler that is a silicate mineral, metal oxide, metal salt, clay, metal silicate, glass fiber, natural fibrous material, synthetic fibrous mineral, or mixtures thereof. In some examples, the additive is an organic filler that is 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, carbon fibers, or mixtures thereof. In some examples, the fillers are present in 0.5-30 percent by weight of the composition. In some examples, the filler comprises at least one flame retardant. In some examples, the at least one flame retardant is an organic phosphate, metal polyphosphate, metal oxide, metal salt, cyanuric acid derivative, or mixtures thereof. In some examples, the at least one flame retardant is present in in 500 to 4000 ppm in the composition.

[0031] In some examples, the composition comprises a foaming agent. In some examples, the foaming agent is at least one of water, pentane, cyclopentane, a hydrofluorocarbon, or mixtures thereof.

[0032] In some examples, the nitro-substituted polyester diols are esters of:

a. oxalic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, C10-dicarboxylic acid, C11-dicarboxylic acid, C12-dicarboxylic acid, C13-dicarboxylic acid, C14-dicarboxylic acid and C15-dicarboxylic acid, and

b. at least one C8-C20 dicarboxylic acid substituted with a single nitro group; and at least one polyol.

[0033] In some examples, the at least one polyol is a C_{1-8} diol.

[0034] In some examples, the composition comprises 20-80% by weight of the nitro-substituted polyester diol.

[0035] In some examples, the composition further comprises the reaction products of
at least one polyester diol not substituted with a nitro group, and
at least one polyisocyanate, and further comprising the reaction product with
at least one chain extender.

[0036] Also provided is a method for making the compositions, comprising reacting:
at least one nitro-substituted polyester diol,
at least one polyisocyanate and
at least one chain extender.

[0037] In some examples, the reaction conditions comprise a temperature of 25 to 120 ^{o}C.

[0038] Also provided is a thermoplastic polyurethane elastomer composition made by the methods described herein.

[0039] In some examples, the thermoplastic polyurethane elastomer composition is 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.

[0040] In some examples, the method further comprises reacting at least one polyester diol not substituted with a nitro group.

[0041] In some examples, the dicarboxylic acids used to make the polyester diol and nitro-polyester diol are esters of:

a. oxalic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, C10-dicarboxylic acid, C11-dicarboxylic acid, C12-dicarboxylic acid, C13-dicarboxylic acid, C14-dicarboxylic acid and C15-dicarboxylic acid, and

b. at least one C8-C20 dicarboxylic acid substituted with a single nitro group; and

at least one diol.

[0042] In some examples, the at least one diol is a C_{1-8} diol.

BRIEF DESCRIPTION OF THE DRAWINGS

[0043] Exemplary embodiments are illustrated in referenced figures. It is intended that the embodiments and figures disclosed herein are to be considered illustrative rather than restrictive.

[0044] **FIG. 1** depicts a bar graph showing the wt% of the dicarboxylic acids in the composition comprising nitro-substituted dicarboxylic acids.

DETAILED DESCRIPTION OF THE INVENTION

[0045] All references cited herein are incorporated by reference in their entirety as though fully set forth. Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs.

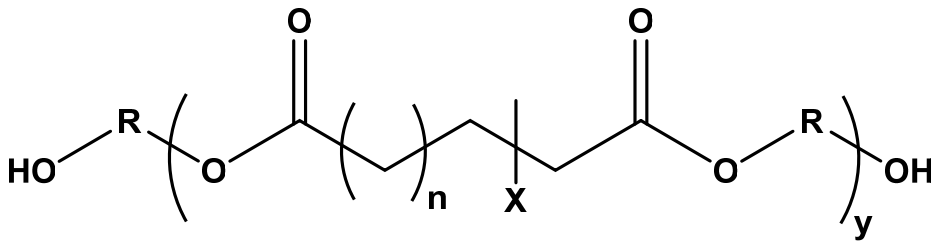
[0046] One skilled in the art will recognize many methods and materials similar or equivalent to those described herein, which could be used in the practice of the present invention. Other features and advantages of the invention will become apparent from the following detailed description, taken in conjunction with the accompanying drawings, which illustrate, by way of example, various features of embodiments of the invention. Indeed, the present invention is in no way limited to the methods and materials described. For convenience, certain terms employed herein, in the specification, examples and appended claims are collected here.

[0047] Unless stated otherwise, or implicit from context, the following terms and phrases include the meanings provided below. Unless explicitly stated otherwise, or apparent from context, the terms and phrases below do not exclude the meaning that the term or phrase has acquired in the art to which it pertains. Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. It should be understood that this invention is not limited to the particular methodology, protocols, and reagents, etc., described herein and as such can vary. The definitions and terminology used herein are

WHAT IS CLAIMED IS:

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

(a) a composition comprising at least one nitro-substituted polyester diol (NO_2-PED), wherein the NO_2-PED is substituted with the nitro group between the two carboxy groups of the NO_2-PED, and at least one polyester diol that is not substituted by a nitro group, wherein the NO_2-PED 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 $C_{1\text{-}8}$ 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.