acid (PLA). More recently, high performance engineering thermoplastics have been used to produce printed articles with improved mechanical and chemical properties relative to common polymer materials. Such high performance thermoplastics include, polyaryletherketones, polyphenylsulfones, polycarbonates, and polyetherimides.

[0010] While additive manufacturing methods can be used to rapidly form an article having any of various shapes and configurations, articles formed by additive manufacturing processes generally suffer from weak adhesion between layers in the z-direction of the printed article. For example, U.S. Patent Application Publication No. 2013/0217838, which related to use of recycled PAEK already used in an SLS process, describes the disadvantages of manufacturing articles from polyaryletherketones using SLS due to poor mechanical performance of the articles in the z-direction of the articles, resulting in anisotropic mechanical properties of the resulting articles.

[0011] While attempts have been made to utilize high performance thermoplastic materials in additive manufacturing and to improve the adhesion between layers of the printed article, there remains a need for additive manufacturing materials that demonstrate improved interlayer adhesion and strength in the z-direction of the article. Further, materials are desired that are capable of use in any of various additive manufacturing processes that provide improved chemical and mechanical properties relative to conventional polymer materials used in additive manufacturing.

BRIEF SUMMARY

[0011a] In one aspect of the present disclosure, there is provided a crosslinkable polymer composition when used ~~for use~~ in an additive manufacturing method, comprising:

at least one aromatic polymer, and at least one crosslinking compound capable of crosslinking the at least one aromatic polymer.

[0011b] In another aspect of the present disclosure, there is provided an article printed by an additive manufacturing process using the crosslinkable polymer composition disclosed herein, wherein the article has at least one of the following properties:

(a) the article has improved interlayer adhesion relative to an article formed by the same additive manufacturing process using an aromatic polymer having the same backbone structure that is not crosslinked; and

(b) the article has improved isotropy in mechanical properties relative to an article formed by the same additive manufacturing process using an aromatic polymer having the same backbone structure that is not crosslinked.

[0011c] In a further aspect of the present disclosure, there is provided a crosslinked composition formed from the composition when used in the additive manufacturing method disclosed herein, ~~having~~ wherein the crosslinked composition has a lower viscosity and a reduced crystallization rate in comparison to a composition formed using the same additive manufacturing method and using ~~of~~ the same aromatic polymer but that is not cross-linked.

[0011d] In another aspect of the present disclosure, there is provided a crosslinked composition formed from the crosslinkable polymer composition when used in the additive manufacturing method disclosed herein, wherein when the method further comprises postcuring of the crosslinked composition into an article, the article has ~~results in~~ improved adhesive bonding between layers

formed from printed filaments or formed by injection molding in comparison to an uncrosslinked composition formed using the same additive manufacturing method and using ~~of~~ the same aromatic polymer.

~~**[0011e]** In another aspect of the present disclosure, there is provided an additive manufacturing composition for use in an additive manufacturing process, wherein the composition comprises a crosslinkable aromatic polymer composition comprising at least one aromatic polymer and at least one crosslinking compound capable of crosslinking the at least one aromatic polymer.~~

[0011e] In another aspect of the present disclosure, there is provided a method for preparing a crosslinkable polymer composition and using it ~~for use~~ in an additive manufacturing method, comprising:

providing at least one aromatic polymer, and at least one crosslinking compound capable of crosslinking the at least one aromatic polymer; ~~and~~

combining the at least one aromatic polymer and the at least one crosslinking compound to form the crosslinkable polymer composition;

using the crosslinkable polymer composition in an additive manufacturing process and crosslinking the at least one aromatic polymer in the crosslinkable polymer composition.

[0011f] In another aspect of the present disclosure, there is provided a crosslinked aromatic polymer ~~for use~~ when used in an additive manufacturing process to form articles which crosslinked aromatic polymer is a reaction product of at least one aromatic polymer and at least one crosslinking compound capable of crosslinking the aromatic polymer.

[0011g] In another aspect of the present disclosure, there is provided a method of preparing an article by an additive manufacturing process, comprising:

p~~P~~roviding the crosslinkable polymer composition used in the method of additive manufacturing disclosed herein; and

utilizing the crosslinkable polymer composition in ~~an~~ the additive manufacturing process to prepare a printed article.

[0011h] In another aspect of the present disclosure, there is provided a method of improving adhesion between layers in an article prepared by an additive manufacturing process, comprising:

providing a crosslinkable aromatic polymer composition comprising at least one aromatic polymer and at least one crosslinking compound capable of crosslinking the at least one aromatic polymer;

introducing the crosslinkable aromatic polymer composition into an additive manufacturing process to prepare a printed article; and

applying heat to the crosslinkable aromatic polymer composition during and/or after the additive manufacturing process to induce crosslinking of the aromatic polymer by the crosslinking compound.

[0011i] In another aspect of the present disclosure, there is provided a method of improving isotropy in mechanical properties of an article prepared by an additive manufacturing process, comprising:

providing a crosslinkable aromatic polymer composition comprising at least one aromatic polymer and at least one crosslinking compound capable of crosslinking the at least one aromatic polymer;

introducing the crosslinkable aromatic polymer composition into an additive manufacturing process to prepare a printed article; and

applying heat to the crosslinkable aromatic polymer composition during and/or after the additive manufacturing process to induce crosslinking of the aromatic polymer by the crosslinking compound.

[0011j] In another aspect of the present disclosure, there is provided a method of improving processability of an aromatic polymer in an additive manufacturing process, comprising:

providing a crosslinkable aromatic polymer composition comprising at least one aromatic polymer and at least one crosslinking compound capable of crosslinking the at least one aromatic polymer; and

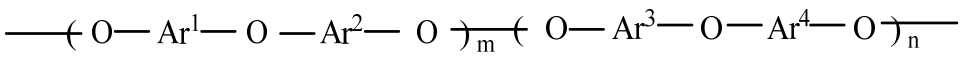
introducing the crosslinkable aromatic polymer composition into an additive manufacturing process to prepare a printed article, whereby the composition exhibits a reduced viscosity in comparison to use of an aromatic polymer composition having the same aromatic polymer but lacking the at least one crosslinking compound.

~~**[0011k]** In another aspect of the present disclosure, there is provided a crosslinked polymer composition for use in an additive manufacturing method, comprising:~~

~~at least one aromatic polymer crosslinked by at least one of thermally-induced crosslinking, grafted crosslinking, and chemical crosslinking.~~

[0012] The present disclosure includes a crosslinkable polymer composition for use in an additive manufacturing methods, comprising: at least one aromatic polymer, and at least one crosslinking compound capable of crosslinking the at least one aromatic polymer.

[0013] The at least one aromatic polymer may be selected from poly(arylene ether)s, polysulfones, polyethersulfones, polyimides, polyamides, polyetherketones, polyphenylene sulfides, polyureas, polyurethanes, polyphthalamide, polyamide-imides, polybenzimidazoles, polyaramids, and blends thereof. The at least one aromatic polymer may further be a poly(arylene ether) including polymer repeating units along its backbone having the structure according to formula (I):



(I)

wherein Ar^1, Ar^2, Ar^3 and Ar^4 are identical or different aryl radicals, m = 0 to 1, and n = 1-m.

CLAIMS

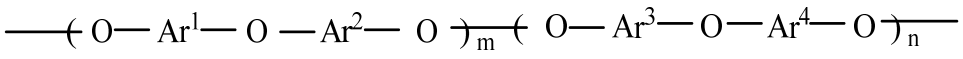
We claim:

1. A crosslinkable polymer composition ~~for~~ when used in an additive manufacturing method, comprising:

at least one aromatic polymer, and at least one crosslinking compound capable of crosslinking the at least one aromatic polymer.

2. The crosslinkable polymer composition when used according to claim 1, wherein the at least one aromatic polymer is selected from poly(arylene ether)s, polysulfones, polyethersulfones, polyimides, polyamides, polyetherketones, polyphenylene sulfides, polyureas, polyurethanes, polyphthalamide, polyamide-imides, polybenzimidazoles, polyaramids, and blends thereof.

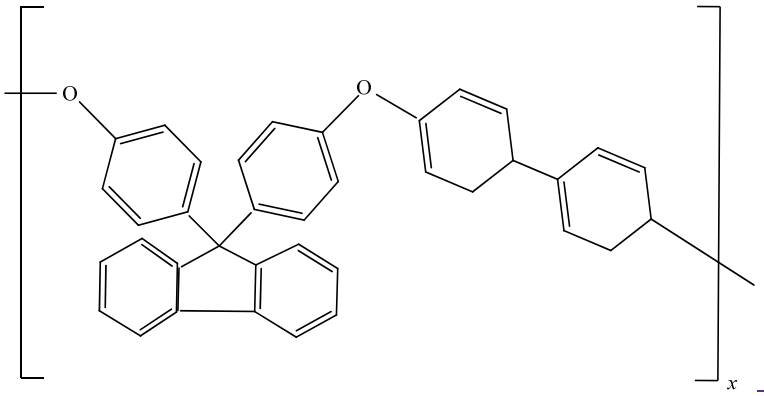
3. The crosslinkable polymer composition when used in the additive manufacturing method according to claim 2, wherein the at least one aromatic polymer is a poly(arylene ether) including polymer repeating units along its backbone having the structure according to formula (I):



(I)

wherein Ar^1, Ar^2, Ar^3 and Ar^4 are identical or different aryl radicals, m = 0 to 1, and n = 1-m.

4. The crosslinkable polymer composition when used in the additive manufacturing method according to claim 3, wherein the at least one aromatic polymer has repeating units along its backbone having the structure of formula (II):

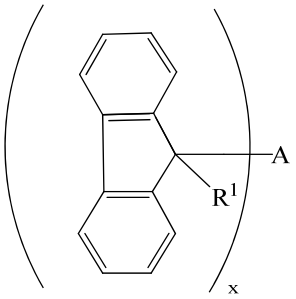


(II).

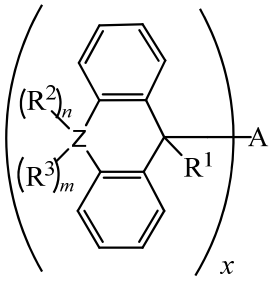
5. The crosslinkable polymer composition when used in the additive manufacturing method according to claim 1, wherein the at least one aromatic polymer is a polyarylene ether or a polyaryletherketone.

6. The crosslinkable polymer composition when used in the additive manufacturing method according to claim 5, wherein the polyaryletherketone is selected from the group of polyetherketone, polyetheretherketone, polyetherketoneketone, and polyetherketoneetherketoneketone.

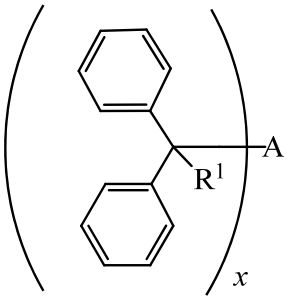
7. The crosslinkable polymer composition when used in the additive manufacturing method according to claim 1, wherein the at least one crosslinking compound has a structure according to one of the following formulae:



(IV) ,



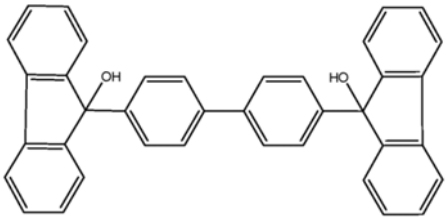
(V) , and

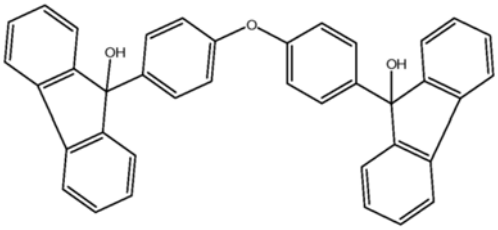


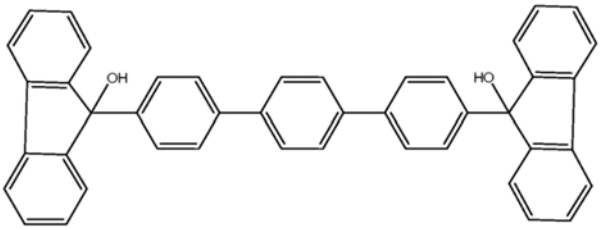
(VI) ,

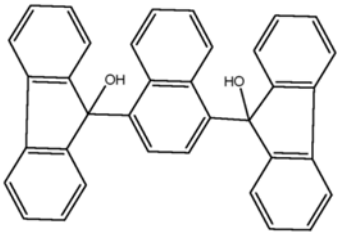
wherein A is a bond, an alkyl, an aryl, or an arene moiety having a molecular weight less than about 10,000 g/mol; wherein R^1, R^2, and R^3 are the same or different and are independently selected from the group consisting of hydrogen, hydroxyl (-OH), amine (NH_2), halide, ester, ether, amide, aryl, arene, or a branched or straight chain, saturated or unsaturated alkyl group of one to about six carbon atoms; wherein *m* is from 0 to 2, *n* is from 0 to 2, and *m* + *n* is greater than or equal to zero and less than or equal to two; wherein *Z* is selected from the group of oxygen, sulfur, nitrogen, and a branched or straight chain, saturated or unsaturated alkyl group of one to about six carbon atoms; and wherein *x* is about 1 to about 6.

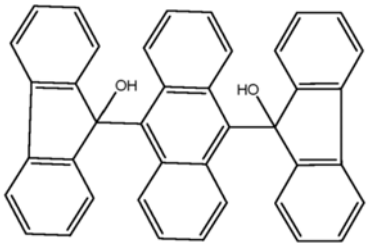
8. The crosslinkable polymer composition when used in the additive manufacturing method according to claim 7, wherein the at least one crosslinking compound has a structure according to formula (IV) and is selected from the group consisting of:

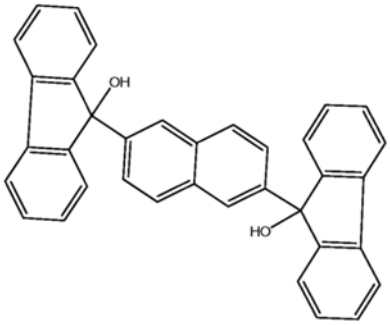


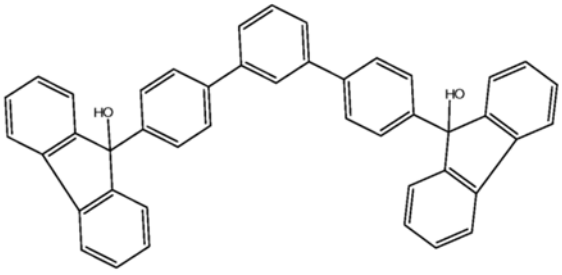
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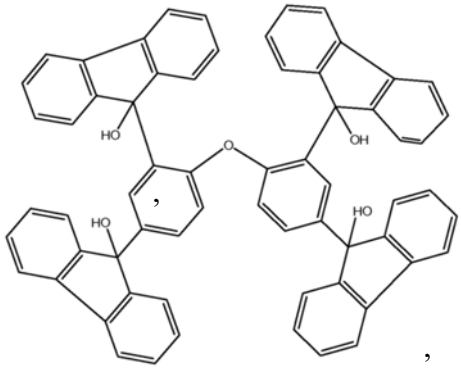
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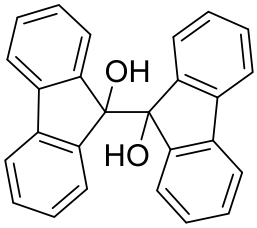
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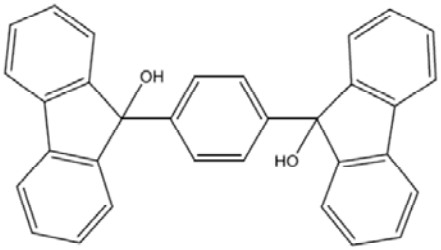
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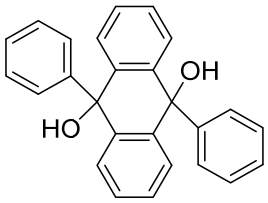
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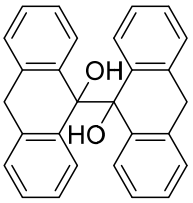


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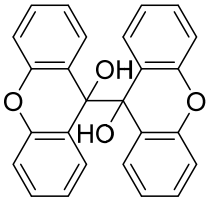
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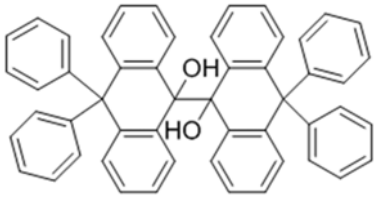
9. The crosslinkable polymer composition when used in the additive manufacturing method according to claim 7, wherein the at least one crosslinking compound has a structure according to formula (V) and is selected from a group consisting of:



, 

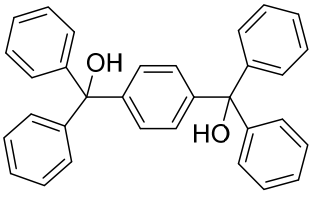
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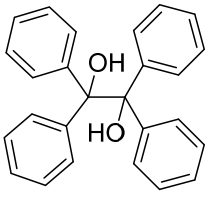


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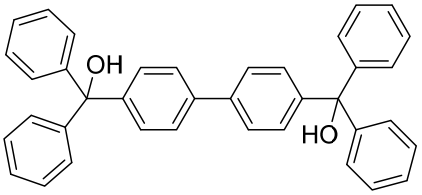
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10. The crosslinkable polymer composition when used in the additive manufacturing method according to claim 7, wherein the at least one crosslinking compound has a structure according to formula (VI) and is selected from the group consisting of:



, 

, and



.

11. The crosslinkable polymer composition when used in the additive manufacturing method according to claim 7, wherein A has a molecular weight of about 1,000 g/mol to about 9,000 g/mol.

12. The crosslinkable polymer composition when used in the additive manufacturing method according to claim 11, wherein A has a molecular weight of about 2,000 g/mol to about 7,000 g/mol.

13. The crosslinkable polymer composition when used in the additive manufacturing method according to claim 1, wherein at least one crosslinking compound is present in the crosslinkable polymer composition in an amount of about 1% by weight to about 50% by weight of an unfilled weight of the crosslinkable polymer composition.

14. The crosslinkable polymer composition when used in the additive manufacturing method according to claim 1, wherein a weight ratio of the aromatic polymer to the crosslinking compound is about 1:1 to about 100:1.

15. The crosslinkable polymer composition when used in the additive manufacturing method according to claim 14, wherein the weight ratio of the aromatic polymer to the crosslinking compound is about 3:1 to about 10:1.

16. The crosslinkable polymer composition when used in the additive manufacturing method according to claim 1, further comprising a crosslinking reaction additive selected from a cure inhibitor and a cure accelerator.

17. The crosslinkable polymer composition when used in the additive manufacturing method according to claim 16, comprising the crosslinking reaction additive in an amount of 0.01% to 5% by weight of the crosslinking compound.

18. The crosslinkable polymer composition when used in the additive manufacturing method according to claim 16, wherein the crosslinking reaction additive is a cure inhibitor and is lithium acetate.

19. The crosslinkable polymer composition when used in the additive manufacturing method according to claim 16, wherein the crosslinking reaction additive is a cure accelerator and is magnesium chloride.

20. The crosslinkable polymer composition when used in the additive manufacturing method according to claim 1, further comprising one or more additives selected from continuous or discontinuous, long or short, reinforcing fibers selected from carbon fibers, glass fibers, woven glass fibers, woven carbon fibers, aramid fibers, boron fibers, polytetrafluoroethylene fibers, ceramic fibers, polyamide fibers; and/or one or more fillers selected from carbon black, silicate, fiberglass, calcium sulfate, boron, ceramic, polyamide, asbestos, fluorographite, aluminum hydroxide, barium sulfate, calcium

carbonate, magnesium carbonate, silica, aluminum nitride, borax (sodium borax), activated carbon, pearlite, zinc terephthalate, graphite, graphene, talc, mica, silicon carbide whiskers or platelets, nanofillers, molybdenum disulfide, fluoropolymer fillers, carbon nanotubes and fullerene tubes.

21. The crosslinkable polymer composition when used in the additive manufacturing method according to claim 20, wherein the polymer composition comprises about 0.5% by weight to about 65% by weight of the one or more additives and/or one or more fillers.

22. An article printed by an additive manufacturing process using the crosslinkable polymer composition according to claim 1~~.~~, wherein the article has at least one of the following properties:

~~23.~~(a) ~~The article of claim 22, wherein~~ the article has improved interlayer adhesion relative to an article formed by the same additive manufacturing process using an aromatic polymer having the same backbone structure that is not crosslinked; and

~~24.~~(b) ~~The article of claim 22, wherein~~ the article has improved isotropy in mechanical properties relative to an article formed by the same additive manufacturing process using an aromatic polymer having the same backbone structure that is not crosslinked.

~~25~~23. The article of claim 22, wherein the additive manufacturing process used to form the article ~~is formed by~~comprises selective laser sintering.

~~26~~24. The article of claim 22, wherein the additive manufacturing process used to form the article ~~is formed by~~comprises fused filament fabrication.

~~27~~25. A crosslinked composition formed from the composition when used in the additive manufacturing method according to claim 1, ~~having~~ wherein the crosslinked composition has a lower viscosity and a reduced crystallization rate in comparison to a composition formed ~~of~~ using the same additive manufacturing method and using the same aromatic polymer but that is not cross-linked.

~~28~~26. ~~The~~ A crosslinked composition formed from the crosslinkable polymer composition when used in the additive manufacturing method according to claim 1, wherein when the method further comprises postcuring of the crosslinked composition into an article, ~~results in~~the article has improved adhesive bonding between layers formed from printed filaments or formed by injection molding in comparison to an uncrosslinked composition formed ~~of~~ using the same additive manufacturing method and using the same aromatic polymer.

~~29. An additive manufacturing composition for use in an additive manufacturing process, wherein the composition comprises a crosslinkable aromatic polymer composition comprising at least one aromatic polymer and at least one crosslinking compound capable of crosslinking the at least one aromatic polymer.~~

~~30~~27. A method for preparing a crosslinkable polymer composition ~~for use~~and using it in an additive manufacturing method, comprising:

providing at least one aromatic polymer, and at least one crosslinking compound capable of crosslinking the at least one aromatic polymer; ~~and~~

combining the at least one aromatic polymer and the at least one crosslinking compound to form the crosslinkable polymer composition;

using the crosslinkable polymer composition in an additive manufacturing process and crosslinking the at least one aromatic polymer in the crosslinkable polymer composition.

~~31~~28. The method according to claim ~~30~~27, further comprising combining the aromatic polymer and the crosslinking compound so the crosslinkable polymer composition is substantially homogeneous.

~~32~~29. The method according to claim ~~30~~27, further comprising combining the aromatic polymer and the crosslinking compound by mechanical blending.

~~33~~30. The method according to claim ~~30~~27, further comprising:

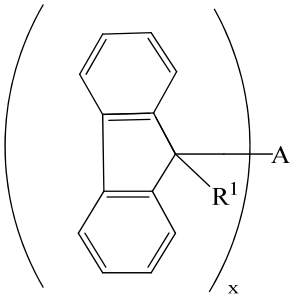
dissolving the aromatic polymer and the crosslinking compound in a common solvent; and

removing the common solvent by evaporation or by addition of a non-solvent so as to cause precipitation of the aromatic polymer and the crosslinking compound out of the common solvent.

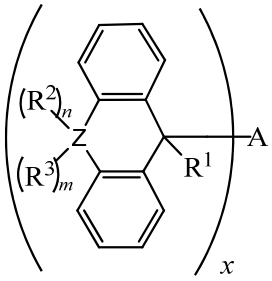
~~34~~31. A crosslinked aromatic polymer ~~for~~ when used in an additive manufacturing process to form articles which crosslinked aromatic polymer is a reaction product of at least one aromatic polymer and at least one crosslinking compound capable of crosslinking the aromatic polymer.

~~35~~32. The crosslinked aromatic polymer when used in an additive manufacturing process to form articles according to claim ~~34~~31, wherein the aromatic polymer is selected from the group of poly(arylene ether)s, polysulfones, polyethersulfones, polyimides, polyamides, polyetherketones, polyphenylene sulfides, polyureas, polyurethanes, polyphthalamides, polyamide-imides, polybenzimidazoles, polyaramids, and blends thereof.

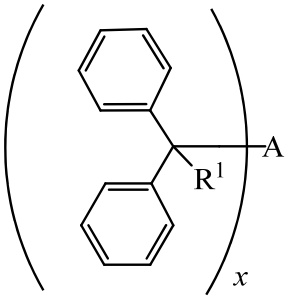
~~36~~33. The crosslinked polymer when used in an additive manufacturing process to form articles according to claim ~~34~~31, wherein the crosslinking compound has a structure according to one of the following formulae:



(IV) ,



(V) , and



(VI) ,

wherein A is bond, an alkyl, an aryl, or an arene moiety having a molecular weight less than about 10,000 g/mol; wherein R^1, R^2, and R^3 are the same or different and are independently selected from the group consisting of hydrogen, hydroxyl (-OH), amine (NH_2), halide, ester, ether, amide, aryl, arene, or a branched or straight chain, saturated or unsaturated alkyl group of one to about six carbon atoms; wherein *m* is from 0 to 2, *n* is from 0 to 2, and *m* + *n* is greater than or equal to zero and less than or equal to two; wherein *Z* is selected from the group of oxygen, sulfur, nitrogen, and a branched or straight chain, saturated or unsaturated alkyl group of one to about six carbon atoms; and wherein *x* is about 1 to about 6.

~~37~~34. A method of preparing an article by an additive manufacturing process, comprising:

providing the crosslinkable polymer composition used in the method of additive manufacturing of claim 1; and

utilizing the crosslinkable polymer composition in ~~an~~ the additive manufacturing process to prepare a printed article.

~~38~~35. The method according to claim ~~37~~34, wherein the additive manufacturing process is a powder bed fusion method.

~~39~~36. The method according to claim ~~37~~34, wherein the additive manufacturing process is a material extrusion method.

~~40~~37. A method of improving adhesion between layers in an article prepared by an additive manufacturing process, comprising:

providing a crosslinkable aromatic polymer composition comprising at least one aromatic polymer and at least one crosslinking compound capable of crosslinking the at least one aromatic polymer;

introducing the crosslinkable aromatic polymer composition into an additive manufacturing process to prepare a printed article; and

applying heat to the crosslinkable aromatic polymer composition during and/or after the additive manufacturing process to induce crosslinking of the aromatic polymer by the crosslinking compound.

~~41~~38. A method of improving isotropy in mechanical properties of an article prepared by an additive manufacturing process, comprising:

providing a crosslinkable aromatic polymer composition comprising at least one aromatic polymer and at least one crosslinking compound capable of crosslinking the at least one aromatic polymer;

introducing the crosslinkable aromatic polymer composition into an additive manufacturing process to prepare a printed article; and

applying heat to the crosslinkable aromatic polymer composition during and/or after the additive manufacturing process to induce crosslinking of the aromatic polymer by the crosslinking compound.

~~42~~39. A method of improving processability of an aromatic polymer in an additive manufacturing process, comprising:

providing a crosslinkable aromatic polymer composition comprising at least one aromatic polymer and at least one crosslinking compound capable of crosslinking the at least one aromatic polymer; and

introducing the crosslinkable aromatic polymer composition into an additive manufacturing process to prepare a printed article, whereby the composition exhibits a reduced viscosity in comparison to use of an aromatic polymer composition having the same aromatic polymer but lacking the at least one crosslinking compound.

~~43~~40. ~~A crosslinked polymer composition for use in an additive manufacturing~~The method according to claim 27, ~~comprising:~~wherein

the at least one aromatic polymer in the crosslinkable polymer composition is crosslinked by at least one of thermally-induced crosslinking, grafted crosslinking, and chemical crosslinking.

~~44. The crosslinked polymer composition for use in an additive manufacturing method according to claim 43, wherein the at least one aromatic polymer is chemically crosslinked and the composition further comprises at least one crosslinking compound capable of crosslinking the at least one aromatic polymer.~~