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 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.

[0011c] In a further aspect of the present disclosure, there is provided a crosslinked composition formed from the composition disclosed herein, having a lower viscosity and a reduced crystallization rate in comparison to a composition formed 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 composition disclosed herein, wherein postcuring of the crosslinked composition into an article results in improved adhesive bonding between layers

formed from printed filaments or formed by injection molding in comparison to an uncrosslinked composition formed 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 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.

[0011f] In another aspect of the present disclosure, there is provided a crosslinked aromatic polymer for use in an additive manufacturing process to form articles which 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:

providing the crosslinkable polymer composition disclosed herein; and

utilizing the crosslinkable polymer composition in an 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

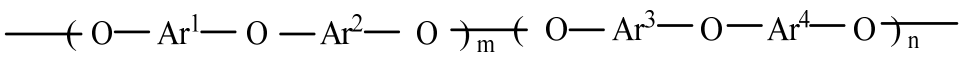
introducing the crosslinkable aromatic polymer composition into an additive manufacturing process to prepare a printed article, whereby the composition exhibits a reduced viscosity in comparison to use of an aromatic polymer composition having the same aromatic polymer but lacking the at least one crosslinking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

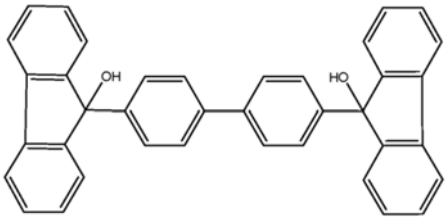


(I)

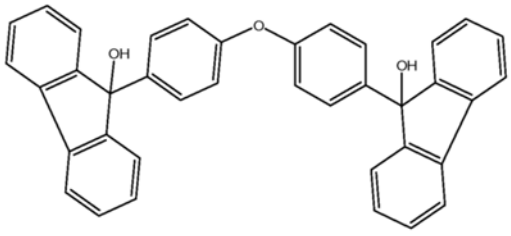
wherein Ar^1, Ar^2, Ar^3 and Ar^4 are identical or different aryl radicals, m = 0 to 1, and n = 1-m.

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.

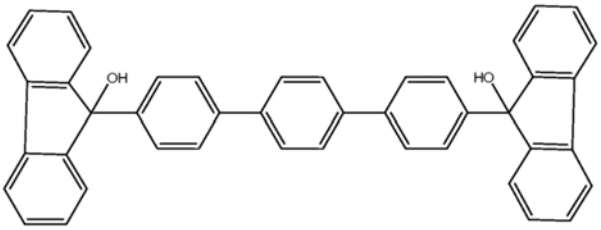
[0015] In one example, the at least one crosslinking compound has a structure according to formula (IV) and is selected from the group consisting of:



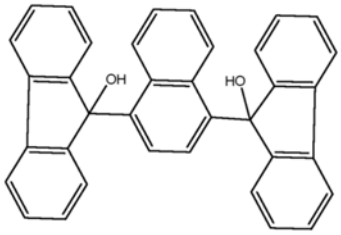
,



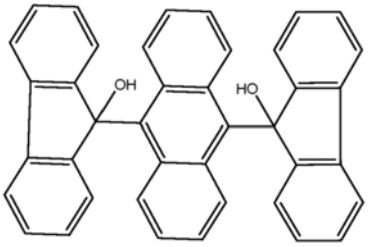
,



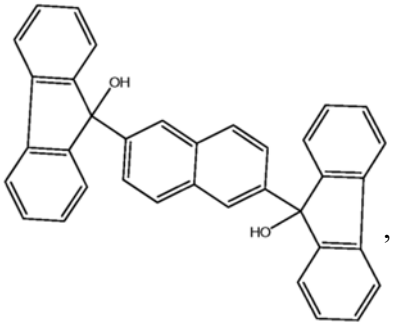
,



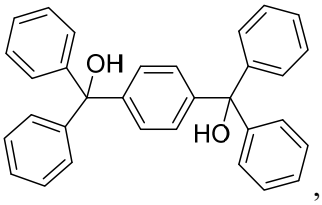
,



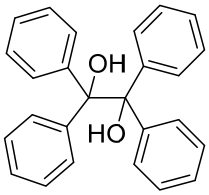
,



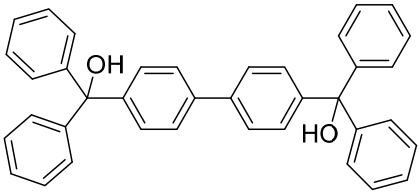
,



,



, and



.

[0018] In a preferred example, A has a molecular weight of about 1,000 g/mol to about 9,000 g/mol, and preferably A has a molecular weight of about 2,000 g/mol to about 7,000 g/mol.

[0019] Preferably, the 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. A weight ratio of the aromatic polymer to the crosslinking compound is preferably about 1:1 to about 100:1, and more preferably the weight ratio of the aromatic polymer to the crosslinking compound is about 3:1 to about 10:1.

[0020] The composition may further comprise a crosslinking reaction additive selected from a cure inhibitor and a cure accelerator. The crosslinking reaction additive may be present in an amount of 0.01% to 5% by weight of the crosslinking compound. The crosslinking reaction additive may be a cure inhibitor such as lithium acetate. The crosslinking reaction additive may also be a cure accelerator such as magnesium chloride.

[0021] One or more additives may be added to the composition such as those 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. The polymer composition in such an example may comprise about

0.5% by weight to about 65% by weight of the one or more additives and/or one or more fillers.

[0022] The compositions noted above when formed into articles result in a lower viscosity and a reduced crystallization rate in comparison to the same aromatic polymers when uncrosslinked, which provides improved processability for the materials when used in additives manufacturing processes such as three-dimensional printing. Further, once postcured, articles formed by the compositions herein result in improved adhesive bonding between layers when formed by printed filaments or by injection molding

[0023] The present disclosure further includes an article printed by an additive manufacturing process using the crosslinkable polymer composition as described above and elsewhere herein. Such an article preferably has improved interlayer adhesion relative to an article formed by an aromatic polymer having the same backbone structure that is not crosslinked. The article preferably also has improved isotropy in mechanical properties relative to an article formed by an aromatic polymer having the same backbone structure that is not crosslinked. In one example, the article is formed by selective laser sintering. In a further example, the article is formed by fused filament fabrication.

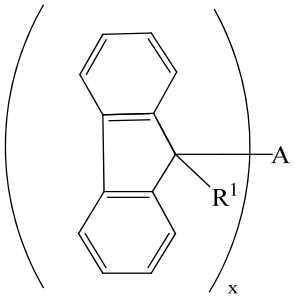
[0024] The present disclosure further incorporates an additive manufacturing composition for use in an additive manufacturing process, wherein the composition comprises a crosslinkable aromatic polymer composition comprising at least one aromatic polymer and at least one crosslinking compound capable of crosslinking the at least one aromatic polymer.

[0025] Also included herein is a method for preparing a crosslinkable polymer composition 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. The method may further comprise combining the aromatic polymer and the crosslinking compound so the crosslinkable polymer composition is substantially homogeneous. In another example, the method may further comprise combining the aromatic polymer and the crosslinking compound by mechanical blending. In yet a further example, the method may comprise: 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.

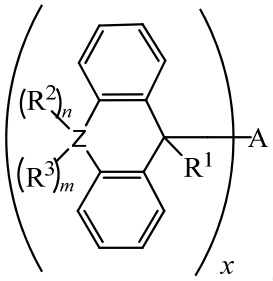
[0026] The present disclosure also includes a crosslinked aromatic polymer for use in an additive manufacturing process to form articles which is a reaction product of at least one aromatic

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

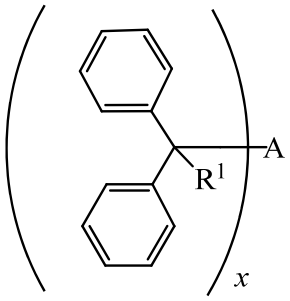
In one example the at least one aromatic polymer is selected from the group of poly(arylene ether)s, polysulfones, polyethersulfones, polyimides, polyamides, polyetherketones, polyphenylene sulfides, polyureas, polyurethanes, polyphthalamides, polyamide-imides, polybenzimidazoles, polyaramids, and blends thereof. 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.

[0027] The present disclosure also includes a method of preparing an article by an additive manufacturing process, comprising: providing the crosslinkable polymer composition of claim 1; and introducing the crosslinkable polymer composition into an additive manufacturing process to prepare a printed article. The additive manufacturing process

may be a powder bed fusion method. The additive manufacturing process may be a material extrusion method.

[0028] A method of improving adhesion between layers in an article prepared by an additive manufacturing process is also included herein which comprises: 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.

[0029] The present disclosure further includes 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.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING(S)

[0030] The foregoing summary, as well as the following detailed description of preferred embodiments of the invention, will be better understood when read in conjunction with the appended drawings. For the purpose of illustrating the invention, there is shown in the drawings embodiments which are presently preferred. It should be understood, however, that the invention is not limited to the precise arrangements and instrumentalities shown. In the drawings:

[0031] Fig. 1 is a representative illustration of the behavior of polymers when printing layers in additive manufacturing for (a) an amorphous polymer; (b) a semicrystalline aromatic polymer such as a PAEK; and (c) a crosslinked aromatic polymer according to the invention;

[0032] Fig. 2 is a graphical representation of the adhesive strength of a crosslinked polyarylene (Arlon 3000XT™) normalized to an uncrosslinked PEEK against bonding pressure as described in Example 1;

[0033] Fig. 3 is a photographic images of crosslinked polyarylene filament formed in according with Example 2;