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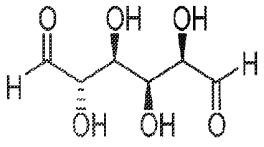

FIG. 1A

(57) Abstract: A polymeric material comprising a base monomer and a multifunctional biobased molecule wherein the multifunctional biobased molecule is a glucose derivative. A polymeric material comprising a base polymer and a polymeric additive comprising glucaric acid, glucodialdose, gluconic acid, erythorbic acid, 2-ketoglucose, lactic acid, adipic acid, sorbitol, glycerol, mannitol, lactones thereof, salts thereof, or combinations thereof wherein the additive when introduced to a base polymer forms a modified polymer wherein the modified polymer has a tensile strength that is increased by from about 10% to about 100% wherein compared to the base polymer.

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BIOBASED COMPOUNDS FOR POLYMER PRODUCTION

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Application Serial No. 63/596,267 filed November 5, 2023 entitled "BIO-BASED COMPOUNDS FOR POLYMER PRODUCTION," which is incorporated herein by reference in its entirety for all purposes.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] Not applicable.

FIELD

[0003] The present disclosure relates generally to the production of polymeric materials. More particularly, this disclosure relates to methods for the production of biobased polymeric materials and applications thereof.

BACKGROUND

[0004] Over the last 150 years, synthesis of inexpensive chemicals from fossilized forms of carbon (e.g. oil, coal, natural gas) has dramatically altered society through the broad applications of such chemicals, ranging from cosmetics to plastics. Such a petroleum-based carbon feedstock generates a small collection of platform chemicals from which highly efficient chemical conversions may be used to prepare of a large variety of chemical products. However, the current approach to producing these carbon-based chemicals is inherently non-sustainable as feedstocks that required millions of years to form are being depleted.

[0005] Polymers are a large class of chemicals derived from petroleum feedstocks. However, an ongoing area of development is the production of biobased polymers. While the terms "biobased polymers" and "biodegradable polymers" are used extensively in the literature, there is a noteworthy difference between the two types of polymers. In particular, biodegradable polymers are defined as polymeric materials whose physical and chemical properties undergo deterioration and completely degrade when exposed to microorganisms, carbon dioxide (aerobic) processes, methane (anaerobic processes), and/or water (aerobic and anaerobic processes). Although biobased polymers can be biodegradable (e.g., polylactic acid) or nondegradable (e.g.,

biopolyethylene), the term "biobased polymers" refers to polymers whose base units are derived from raw materials such as plants and other renewable agricultural, marine, and forestry materials.

[0006] For example, polyamide polymers such as Nylon cannot be fully degraded or chemically recycled back to its constituent monomers without energy intensive processes. Currently nylons are mainly made up of adipic acid and hexamethylenediamine (HMDA) and articles made from nylon characteristically exhibit high strength, and chemical resistance. While these properties are desired for a variety of commercial products, these materials suffer from drawbacks such as poor to no recyclability. It would be desirable to have a green alternative where the raw materials for polymer production will not depend on petrochemical feedstocks.

SUMMARY

[0007] In some aspects, disclosed herein is a polymeric material may comprises a base polymer and a multifunctional biobased molecule. The multifunctional biobased molecule may be a glucose derivative.

[0008] Also, in some aspects, disclosed herein is a polymeric material comprising a base polymer and a polymeric additive comprising glucaric acid, glucodialdose, gluconic acid, erythorbic acid, 2-ketoglucose, lactic acid, adipic acid, sorbitol, glycerol, mannitol, lactones thereof, salts thereof, or combinations thereof. When the additive is contacted with a base polymer, a modified polymer may be formed. The modified polymer may exhibit a tensile strength that is increased by from about 10% to about 100% in comparison to the base polymer.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] For a detailed description of various exemplary embodiments, reference will now be made to the accompanying drawings in which:

[0010] Figure 1A depicts the chemical structure of glucodialdose.

[0011] Figure 1B depicts the chemical structure of glucodiamine.

[0012] Figure 1C depicts the chemical structure of and glucaric acid.

[0013] Figure 1D depicts the chemical structure of glucaramide.

[0014] Figure 1E depicts the chemical structure of gluconamide.

[0015] Figure 2 depicts the chemical conversion of glucose to a glucohexadialdose intermediation that is subsequently converted to reaction products.

[0016] Figure 3 depicts the reaction of diamines with either diacyl chlorides or diacids to form polyamides.

[0017] Figure 4 depicts the reaction of various diamines with either a diacid or diacyl chloride to produce polyamides.

[0018] Figure 5A depicts the reaction of glucodialdose with two equivalents of phenol to form a polyphenol.

[0019] Figure 5B depicts the reaction of glucaric acid to form a variety of intermediates,

[0020] Figure 5C depicts the reaction of furandicarboxylic acid with ethylene glycol to form polyethylene furanoate.

[0021] Figure 5D depicts the reaction of gluconate and a diamine to form a polyamide.

[0022] Figure 6 presents the Fourier transform infrared spectra (FTIR) for the reagents and reaction product in the acid catalyzed addition of phenol, glucose and glucodialdose

[0023] Figure 7 presents the structures of different products from Example 3.

[0024] Figure 8 depicts the reaction of gluonic acid and urea to form a polymer and the FTIR spectra of the reagents and reaction product.

DETAILED DESCRIPTION

[0025] The following discussion is directed to various exemplary aspects. However, one of ordinary skill in the art will understand that the examples disclosed herein have broad application, and that the discussion of any aspect is meant only to be exemplary of that aspect, and not intended to suggest that the scope of the disclosure, including the claims, is limited to that aspect.

[0026] The figures are not necessarily to scale. Certain features and components herein may be shown exaggerated in scale or in somewhat schematic form and some details of conventional elements may not be shown in interest of clarity and conciseness.

[0027] In the following discussion and in the claims, the terms "including" and "comprising" are used in an open-ended fashion, and thus should be interpreted to mean "including, but not limited to... ." As used herein, the terms "approximately," "about," "substantially," and the like mean within 10% (i.e., plus or minus 10%) of the recited value. Thus, for example, a recited angle of "about 80 degrees" refers to an angle ranging from 72 degrees to 88 degrees.

[0028] Unless the context dictates the contrary, all ranges set forth herein should be interpreted as being inclusive of their endpoints, and open-ended ranges should be interpreted to include only commercially practical values. Similarly, all lists of values

should be considered as inclusive of intermediate values unless the context indicates the contrary.

[0029] Disclosed herein are multifunctional biobased molecules for use in the production or modification of polymeric materials. In one or more aspects, the multifunctional biobased molecule may function to alter one or more of the properties associated with a base polymeric materials. In one or more aspects, the multifunctional biobased molecules are used as a monomer that forms a homopolymer or as a comonomer to form a copolymer. In some aspects, the multifunctional biobased molecules comprise equal to or greater than about 70% of the carbon atoms derived from a compound that is obtained from a renewable resource; additionally or alternatively, equal to or greater than about 75%, 80%, 85%, 90%, 95%, or 100% of the carbons derived from a renewable resource. Hereinafter the multifunctional biobased molecules are designated MBMs.

[0030] In one or more aspects, the MBM is a sugar derivative. For example, the MBM may be derived from a monosaccharide such as glucose, fructose or galactose, or a disaccharide such as sucrose or lactose. In an aspect, the MBM is a sugar oxidation product or a product derived from a sugar oxidation product.

[0031] In one or more other aspects, the MBM is a nitrogen-containing compound a sugar oxidation product derivative. In some aspects, the one or more sugar oxidation products comprise a glucose oxidation product, a gluconic acid oxidation product, a gluconate, or combinations thereof. The glucose oxidation product, gluconic acid oxidation product, or combination thereof may be buffered to a suitable pH.

[0032] Additionally or alternatively, the one or more sugar oxidation products comprise glucaric acid, gluconic acid, glucuronic acid, glucose oxidation products, gluconic acid oxidation products, or combinations thereof.

[0033] Additionally or alternatively, the one or more sugar oxidation products comprise galactonic acid, galactaric acid, an oxidation product comprising predominantly (e.g., greater than about 50 wt.%) galactonic acid and/or galactaric acid with minor component species of n-keto-acids, C2 to C6 diacids, or combinations thereof, for example, which may be present in an amount less than about 10 wt.%, additionally or alternatively, less than about 5 wt.% percent, additionally or alternatively, from about 1 wt.% percent to about 10 wt. %. Additionally or alternatively, in one or more aspects, the one or more sugar oxidation products comprise glutamic acid. Additionally or alternatively, the one

or more sugar oxidation products comprise glucodialdose, 2-ketoglucose, or combinations thereof.

[0034] In an aspect, the one or more one or more sugar oxidation products suitable for use in the present disclosure comprise less than about 5 wt.% maltose, maltotriose, fructose, higher molecular weight polysaccharides, oxidation products thereof, or combinations thereof based on the total weight of the sugar-derived carboxylic acid.

[0035] In one or more aspects, the nitrogen-containing compound is derived from glucaric acid, glucodialdose or both. Nonlimiting examples of MBMs sourced from a sugar oxidation product include glucodiamine, gluconamide, glucaramide or combinations thereof. The chemical structures of glucodialdose, glucodiamine, glucaric acid, glucaro diamide, and glucono amide are depicted in Structures 1A, 1B, 1C, 1D and 1E, respectively.

[0036] In some aspects, the sugar oxidation products and/or MBMs are produced using processes involving enzymatic catalysts, metal-containing catalysts or combinations thereof. In one or more aspects, the sugar oxidation products and/or MBMs are not derived from petroleum feedstocks.

[0037] In one or more aspects, a method of producing an MBM comprises the oxidation of glucose to form glucohexadialdose (glucodialdose) which can then be reacted to form an MBM such as glucaric acid, gluconamide, glucodiamine, glucaramide or combinations thereof. This reaction is depicted in Figure 2.

[0038] In one or more aspects, the MBM may be effective to increase the biodegradability and/or recyclability of another polymer. For example, the MBM may be contacted with a base polymer (e.g. polyamide) such that the resultant copolymer exhibits an increased level biodegradable units allowing for deconstruction of the polymer at the end of product life over a shorter time period and/or utilizing less energy.

[0039] In some aspects, the MBM is introduced into a polymer production process in a manner that allows the MBM to uniformly distributed throughout at least a portion of the copolymer. In some aspects, the MBM is introduced into a polymer production process in a manner that allows the MBM to distributed randomly throughout at least a portion of the copolymer. For example, letting X represent the base monomer and Y represent the MBM, the copolymer may have the MBM distributed uniformly (e.g., XXXYXXXYXXXY) or randomly (e.g., XYXXXYYXXXXYXXY). In some aspects, the MBM is introduced into the polymer production process to allow for MBM to comprise a

portion of the backbone of the copolymer. The copolymer comprising the MBM may vary in chain length and structure from the base polymer.

[0040] The amount of MBM present in the copolymer may range from about 1 weight percent (wt.%) to about 90 wt.% based on the total weight of the copolymer or about 1 wt.% to about 10 wt.% or from about 1 wt.% to about 50 wt.% or from about 1 wt.% to about 20 wt.%. It is contemplated that the amount of MBM introduced will depend on a number of factors including the desired characteristics and intended application of the polymer. A copolymer comprising a base polymer and the MBM may have a biodegradability that is increased by from about 5% to about 100% or from about 10% to about 90% or from about 25% to about 75% or from about 40% to about 60% or about 50% when compared to the biodegradability of the base polymer. Biodegradability may be measured using any suitable methodology for measuring plastic biodegradability for example ISO 17556, ISO 14853 or ASTM D5988-18.

[0041] In an aspect, a diamine and a diacid or a diamine and a diacyl chloride are reacted under conditions suitable for formation of a polyamide. For example, with reference to Figure 3, a diamine characterized by any of general structures A through E may be reacted with a diacyl chloride such as exemplified by general structure F under conditions suitable for the formation of a polyamide. Referring to Figure 3, in the alternative, a diamine characterized by any of general structures A through E may be reacted with a diacid such as exemplified by any of general structures G through J under conditions suitable for the formation of a polyamide. In the alternative and with reference to Figure 4, a diamine characterized by any of general structures K through M may be reacted with a diacyl chloride such as exemplified by general structure N or diacid as exemplified by general structure O under conditions suitable for the formation of a polyamide such as exemplified by general structures P, Q and R. With reference to Figures 3 and 4, each R may independently be hydrogen, methyl, C_xH_{2x+1}, Tr, or B_n and each R' may each independently be a C_2, C_4, or C_6 group that is aromatic, saturated or unsaturated.

[0042] In one or more aspects, the MBM comprises glucodialdose and is used in the production of resins such as polyphenols or polyureas. For example, glucodialdose may reacted with two equivalents of a phenol in the presence of an acid catalyst (e.g., H_2SO_4) and at an elevated temperature (e.g., greater than about 100 °F) to form a polyphenol; this is depicted schematically in Figure 5A.

[0043] In one or more aspects, glucaric acid is a sugar oxidation product that serves as an MBM and can be used in the formation of polymers such as polyesters and polyamides. These reactions are depicted schematically in Figure 5B. In some aspects, glucaric acid can used in the formation of 2,5-furandicarboxylic acid (FDCA) and/or glucaric acid dilactone which is 1,4:6,3 dilactone (GAdL). GAdL may function as a MBM. In an aspect, FDCA is reacted by polycondensation with ethylene glycol to generate polyethylene furanoate (PEF). These reactions are depicted schematically in Figure 5C.

[0044] In an aspect, the MBM comprises a glucaric acid based polymer (e.g., a polyglucaramide) that is used in the formation of a hydrogel. Hydrophilic gels (hydrogels) are networks of polymer chains that are sometimes found as colloidal gels in which water is the dispersion medium. Hydrogels exhibit a vast array of usability results from their ability to absorb and retain proportionally large quantities of water, versatile mechanical and physico-chemical properties, and excellent biocompatibility. In one or more aspects, a method of the present disclosure comprises polycondensation of a gluconate with a diamine to form a polyglucaramide. This reaction is depicted schematically in Figure 5D. Polyglucaramides contain hydroxyl and amide functional groups that can crosslink to form a gel or a hydrogel.

[0045] In one or more aspects, the MBM comprises gluconate and is used in the production of a polyamide (e.g., Nylon) from an amide monomer. In such aspects, the MBM is reacted with a diamine under conditions suitable for the formation of a polyamide. This reaction is depicted schematically in Figure 5D.

[0046] In one or more aspects, the MBM comprises glucodiamine and is used in the production of a polyamide (e.g., Nylon). In one or more aspects, the MBM comprises glucodialdose and is used in the production of a polyamide copolymer (e.g., Nylon). In one or more aspects, the MBM comprises glucaramide and is used in the production of a polyamide copolymer (e.g., Nylon). In one or more aspects, the MBM comprises gluconamide and is used in the production of a polyamide copolymer (e.g., Nylon). In one or more aspects, the MBM comprises a mixture of glucaramides and gluconamides and is used in the production of a polyamide copolymer (e.g., Nylon). In such aspects, the mixture of glucaramides and gluconamides has a ratio of glucaramides to gluconamides of from about 0.1:10 to about 10:0.1, additionally or alternatively, about 1:10 to about 10:1, additionally or alternatively, about 2:10 to about 10:2, additionally or alternatively, about 3:10 to about 10:3, additionally or alternatively, about 1:2 to about 2:1 or, additionally or alternatively, about 1:1. In one or more aspects, the MBM

comprises a mixture of glucodialdose and glucodiamine and is used in the production of a polyamide copolymer (e.g., Nylon). In such aspects, the mixture of glucodialdose and glucodiamine has a ratio glucodialdose to glucodiamine of from about 0.1:10 to about 10:0.1, additionally or alternatively, about 1:10 to about 10:1, additionally or alternatively, about 2:10 to about 10:2, additionally or alternatively, about 3:10 to about 10:3, additionally or alternatively, about 1:2 to about 2:1 or, additionally or alternatively, about 1:1. In one or more aspects, the MBM comprises a mixture of glucodialdose and glucodiamine and is used in the production of a polyamide copolymer (e.g., Nylon). In such aspects, the mixture of glucodialdose and glucodiamine has a ratio glucodialdose to glucodiamine of from about 0.1:10 to about 10:0.1, additionally or alternatively, about 1:10 to about 10:1, additionally or alternatively, about 2:10 to about 10:2, additionally or alternatively, about 3:10 to about 10:3, additionally or alternatively, about 1:2 to about 2:1 or, additionally or alternatively, about 1:1. In one or more aspects, the MBM comprises a mixture of glucaric acid and glucodiamine and is used in the production of a polyamide copolymer (e.g., Nylon). In such aspects, the mixture of glucaric acid and glucodiamine has a ratio glucaric acid to glucodiamine of from about 0.1:10 to about 10:0.1, additionally or alternatively about 1:10 to about 10:1, additionally or alternatively, about 2:10 to about 10:2, additionally or alternatively, about 3:10 to about 10:3, additionally or alternatively, about 1:2 to about 2:1 or, additionally or alternatively, about 1:1. An MBM may be a component of a polyamide polymer and may be introduced using any suitable methodology. For example, when a MBM is used in the production of a polyamide copolymer, the polyamide-MBM copolymer may be formed by the condensation of HMDA, and adipic acid in the presence of the MBM. Alternatively, the MBM can be contacted with the polyamide polymer after pelletization of the polymer such as by extrusion.

[0047] In an aspect, a method the present disclosure comprises acetylation of a MBM. For example, the MBM may comprise glucaric acid. In another aspect, the MBM comprises glucodiamine. In yet another aspect, the MBM comprises glucaric acid and glucodiamine. A method of the present disclosure further comprises polymerizing the acetylated glucaric acid and glucodiamine to form a polymeric amide material (PAM).

[0048] In an aspect, a PAM of the present disclosure is characterized by an increased rigidity when compared to Nylon 6,6. A PAM of the present disclosure may be further characterized by an increased hydrophobicity when compared to Nylon 6,6 such than an article formed from the PAM may exhibit an increased water resistance so as to

provide a water-resistant article such as clothing. A PAM of the present disclosure may be further characterized by an increased biodegradability when compared to Nylon 6,6 and the PAM may be hydrolyzed under acidic conditions. In an aspect, a PAM of this disclosure may be purified by distillation. The PAM may have a purity via distillation of equal to or greater than about 90%, alternatively equal to or greater than about 95%, alternatively equal to or greater than about 98%, or alternatively equal to or greater than about 99%.

[0049] In one or more aspects, the base polymer is a polyurethane polymer and the copolymer is an MBM. Polyurethane is a general term used for a class of polymers derived from the condensation of polyisocyanates and polyalcohols and they can be easily synthesized through an addition reaction between alcohol and an isocyanate. The polyurethane-MBM copolymer may be formed by the condensation of one or more polyisocyanates and one or more polyalcohols in the presence of the MBM.

[0050] In one or more aspects, the base polymer is a polyurethane polymer and the copolymer is an MBM. Polyurethane is a general term used for a class of polymers derived from the condensation of polyisocyanates and polyalcohols. and they can be easily synthesized through an addition reaction between alcohol and an isocyanate. The polyurethane-MBM copolymer may be formed by the condensation of one or more polyisocyanates and one or more polyalcohols in the presence of the MBM.

[0051] In one or more aspects, the base polymer is a polyester polymer and the copolymer is an MBM. A polyester refers to a type of polymer formed through a condensation reaction between a dicarboxylic acid and a diol, creating long chains of repeating ester linkages, (e.g., polyethylene terephthalate (PET)). The polyester-MBM copolymer may be formed by the condensation of one or more dicarboxylic acids and one or more polyols in the presence of the MBM.

[0052] In one or more aspects, any copolymer disclosed herein further includes a functionalizing additive. The functionalizing additive may provide additional and/or new chemical moieties to the copolymer that alters one or more characteristics of the copolymer. Nonlimiting examples of functionalizing additives that may be used include erythorbic acid, lactic acid, succinic acid, tartaric acid and nonglucose-based diamines, derivatives thereof and combinations thereof. The functionalizing additive may be included in the copolymer using any suitable methodology such as being introduced during the polymerization process or being introduced via a process step such as reactive extrusion. The functionalizing additive may be present in the copolymer in

amounts ranging from about 0.1 weight percent (wt.%) to about 10 wt.% based on the total weight of the copolymer or from about 0.5 wt.% to about 7.5 wt.% or from about 1 wt.% to about 6 wt.% or from about 2 wt.% to from about 5 wt.% or from about 2 wt.% to about 4 wt.%.

[0053] In one or more aspects, the MBM functions as a polymer additive. In such aspects the MBM may be included to alter one or more characteristics of the final polymer product. In such aspects, the MBM additive functions to improve mechanical properties of the final polymer product. In one or more aspects, the MBM additive comprises glucaric acid, glucodialdose, gluconic acid, erythorbic acid, 2-ketoglucose, lactic acid, adipic acid, sorbitol, glycerol, mannitol, lactones thereof, salts thereof, or combinations thereof.

[0054] For example, the MBM may function to improve the strength of the polymer product.

[0055] Impacts of the MBM on the polymer strength may be evidenced by increases in polymer tensile strength ranging from about 10% to about 100% or about 25% to about 75% of about 50% when compared to the polymer strength in the absence of the MBM additive. Tensile strength may be measured in accordance with any suitable methodology, for example in accordance with ASTM D638.

[0056] When the additive is contacted with a base polymer, a modified polymer is formed. The modified polymer may have a tensile strength that is increased by from about 10% to about 100% wherein compared to the base polymer. In one or more aspects, the MBM additive functions a strengthening agent in the preparation of polymers such as a polyester, polyurethane or polylactic acid.

[0057] In other aspects, the MBM additive may alter the structure of the polymer by increasing polymer branching. Herein polymer branching refers to the occurrence of side chains or branches of various lengths originating at random points from a single linear polymer chain. The type and extent of these side chains in a polymer impacts a multitude of polymer properties such as density, strength, crystallinity, and melting points. In one or more aspects, the MBM additive functions as a branching agent in the preparation of polymers such as a polyester or polyurethane.

[0058] In one or more aspects, the MBM additive may function as a polymer plasticizer. Polymer plasticizers improve the flexibility, workability, and processability of polymers by acting as a lubricant between polymer chains allowing the chains to move freely. In

one or more aspects, the MBM additive is used as a polymer plasticizer with a water soluble polymer such as polyvinyl alcohol, polyacrylamide and polyethylene oxide.

[0059] The MBM additive may be included in a base polymer to form a modified polymer using any suitable methodology such as being introduced during the base polymer polymerization process or being introduced via subsequent to polymerization of the base polymer such as through extrusion. The functionalizing additive may be present in the modified polymer in amounts ranging from about 0.1 weight percent (wt.%) to about 10 wt.% based on the total weight of the copolymer, additionally or alternatively, from about 0.5 wt.% to about 7.5 wt.% or from about 1 wt.% to about 6 wt.%, additionally or alternatively, from about 2 wt.% to from about 5 wt.% or, additionally or alternatively, from about 2 wt.% to about 4 wt.%.

[0060] Disclosed herein are MBMs that may be useful in applications including, but not limited to, the production of woven fibers (e.g., carpets, textile, molded parts, clothes and recycling); the production of construction fibers (e.g., fiberglass replacement, carbon fiber replacement, mineral wool); as insulation (e.g., automotive heat insulation, electroinsulation, pipes); as polymer additives (e.g., plasticizer, anti-plasticizer); and as property-modifying additives (e.g., improve mechanical strength, thermal stability, moisture absorption, chemical resistance in plastics).

[0061] In one or more aspects, the MBM comprises glucaric acid, gluconic acid, glucodiamine, glucodialdose, 2-ketoglucose, one or more salts thereof, one or more derivatives thereof, or combinations thereof. The MBM may function as a monomeric compound that, under suitable conditions, forms a polymeric molecule displaying desirable mechanical and/or physical properties such as a high glass transition temperature, increased tensile strength, improved Young's modulus, corrosion resistance, permeability, or combinations thereof.

[0062] In another aspect, a MBM of the present disclosure may function as a comonomer to produce a polymeric compound (e.g., copolymer, terpolymer) having n differing monomers where n ranges from 1 to 10, additionally or alternatively, from 1 to 5. In such aspects, the MBM may be a comonomer that is included with any other suitable monomer to form a copolymer having any suitable structure such as a linear copolymer, grafted copolymer, block copolymer, or the like. For example, the MBM may form a copolymer with monomers such as ethylene, propylene, styrene, tetrafluoroethylene, vinyl chloride, lactic acid, phenol-formaldehyde, or acrylonitrile.

[0063] In an aspect, the MBMs provide a sustainable source of amine production that are not solely dependent on a petroleum-based adiponitrile production. Additionally, the MBM provides a green alternative with potential benefits to environments (i.e. biodegradability, toxicity) and recycling features (i.e. shoes, clothes, furniture, wood, plastic recycling).

[0064] The present disclosure contemplates the use of bio-based adipic acid and/or bio-based HDMA, for production of a biodegradable, recyclable, biobased polyamide Nylon product including but not restricted to Nylon 6, 6. In one or more aspects, the biobased compounds of the present disclosure are prepared from renewable feedstocks such as sugars. It is contemplated that MBMs and other sugar-derived molecules may function in lieu of fossil-fuel based polymer reactants or polymer additives.

ADDITIONAL DISCLOSURE

[0065] A first aspect which is a polymeric material comprising a base monomer and a multifunctional biobased molecule wherein the multifunctional biobased molecule is a glucose derivative.

[0066] A second aspect which is the polymeric material of the first aspect wherein the glucose derivative is a sugar oxidation product.

[0067] A third aspect which is the polymeric material of any of the first through second aspects wherein the glucose derivative comprises glucaric acid, gluconic acid, glucuronic acid, galactonic acid and/or galactaric acid with minor component species of n-keto-acids, C2 to C6 diacids, glutamic acid glucodialdose, 2-ketoglucose, or combinations thereof.

[0068] A fourth aspect which is the polymeric material of any of the first through third aspects wherein the multifunctional biobased molecule comprises glucodiamine, gluconamide, glucaramide glucohexadialdose glucaric acid, gluconic acid, 1,4:6,3 glucaric acid dilactone or combinations thereof.

[0069] A fifth aspect which is the polymeric material of any of the first through fourth aspects wherein the base monomer comprises an amide, an ester, an ethylene, a urethane, a henol or combinations thereof,

[0070] A sixth aspect which is the polymeric material of any of the first through fifth aspects wherein the multifunctional biobased molecule is present in an amount of from about 1 wt.% to about 90 wt.% based on the total weight of the polymeric material.

[0071] A seventh aspect which is the polymeric material of any of the first through sixth aspects wherein the polymeric material has a biodegradability that is increased by from about 5% to about 100% when compared to the base polymer.

[0072] An eighth aspect which is the polymeric material of any of the first through seventh aspects wherein the base monomer comprises a phenol and the multifunctional biobased additive comprises glucodialdose.

[0073] A ninth aspect which is the polymeric material of any of the first through eighth aspects wherein the base monomer comprises an amide and the multifunctional biobased additive comprises glucodialdose.

[0074] A tenth aspect which is the polymeric material of any of the first through ninth aspects wherein the base monomer comprises an amide and the multifunctional biobased additive comprises glucaro diamide.

[0075] An eleventh aspect which is the polymeric material of any of the first through tenth aspects wherein the base monomer comprises an amide and the multifunctional biobased additive comprises glucono amide.

[0076] A twelfth aspect which is the polymeric material of any of the first through eleventh aspects wherein the base monomer comprises a polyamide and the multifunctional biobased additive comprises a mixture of glucaro dimides and glucono amides.

[0077] A thirteenth aspect which is the polymeric material of any of the first through twelfth aspects wherein the base monomer comprises an amide and the multifunctional biobased additive comprises a mixture of glucodialdose and glucodiamine

[0078] A fourteenth aspect which is the polymeric material of any of the first through thirteenth aspects wherein the base monomer comprises an amide and the multifunctional biobased additive comprises a mixture of glucaric acid and glucodiamine.

[0079] A fifteenth aspect which is the polymeric material of any of the first through fourteenth aspects further comprising erythorbic acid, lactic acid, adipic acid, sorbitol, glycerol, mannitol, lactones thereof, salts thereof, or combinations thereof.

[0080] A sixteenth aspect which is a polymeric material comprising a base polymer and a polymeric additive comprising glucaric acid, glucodialdose, gluconic acid, erythorbic acid, 2-ketoglucose, lactic acid, adipic acid, sorbitol, glycerol, mannitol, lactones thereof, salts thereof, or combinations thereof wherein the additive when contacted with a base polymer forms a modified polymer wherein the modified polymer has a tensile strength

that is increased by from about 10% to about 100% wherein compared to the base polymer.

[0081] A seventeenth aspect which is the polymeric material of the sixteenth aspect wherein the base polymer comprises a polyester.

[0082] An eighteenth aspect which is the polymeric material of any of the sixteenth through seventeenth aspects wherein the base polymer comprises a polylactic acid.

[0083] A nineteenth aspect which is the polymeric material of any of the sixteenth through nineteenth aspects wherein the base polymer comprises polyurethane.

[0084] A twentieth aspect which is a hydrogel comprising the polymeric material of any preceding aspects.

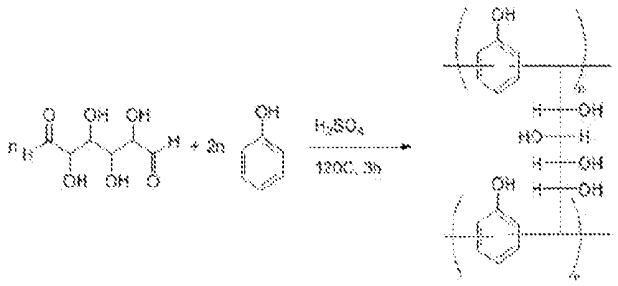
EXAMPLES

[0085] The aspects having been generally described, the following examples are given as particular aspects of the disclosure and to demonstrate the practice and advantages thereof. It is understood that the examples are given by way of illustration and are not intended to limit the specification or the claims in any manner.

EXAMPLE 1

[0086] An MGM, gluodiamine, was used in the preparation of a polymer. The reaction is depicted in Equation 1

(Equation 1)



Glucodialdose (4.5 g, 1 equivalent) and phenol (9.4g, 2 equivalents) were mixed and the temperature elevated to 120 °C before the addition of H_2SO_4 as the reaction catalyst. The reaction was stirred for 3 hours before cooling to 60 °C. NaOH (1.7 ml of a 1M solution) was added to neutralize the cooled mixture. Water was removed (approximately 60%) from the reaction mixture by rotovaping. The resulting product can be cured using any suitable curing agent. The product was identified using FTIR which indicated the presence of aldehyde at 1700 cm^{-1}, a change in aromatic content at 1500 cm^{-1}.

EXAMPLE 2

[0087] Phenol resins was prepared by acid catalyzed addition of phenol with glucose for a reaction time ranging from about 15-20 minutes. Glucodialdose (GDA) was then added. The weight percent of glucose and glucodialdose based on the total resin weight are indicated in Table 1. The reaction was neutralized with sodium hydroxide. The final product had an increased solubility in water with the addition of as little as 5% GDA demonstrating the MBM functioned as a crosslinker. The reaction is depicted schematically in Figure 7. A comparison of the reagent Fourier transform infrared spectra (FTIR) for the reagents and products is presented in Figure 6.

Table 1

Total MGM concentration	Glucose	Glucodialdose
0	2.49	0
5	2.37	0.12
10	2.24	0.25
25	1.87	0.62
50	1.25	1.25
75	0.62	1.87

EXAMPLE 3

[0088] Urea resins was prepared addition of phenol with glucose at a temperature of 75 °C for 3 hours in water. The reaction mixture was clear and the product was a sticky solid. Fourier transform infrared spectra (FTIR) for the reagents and products is presented in Figure 8.

EXAMPLE 4

[0089] The esterification of glucaric acid was carried out using 403.26 mmol of glucaric acid, and 10.4 mol of butanol in the presence of 27 mol% of sulfuric acid. The reaction mixture was refluxed for between 2 to 4 hours to form an esterified glucaric acid.

[0090] The subject matter having been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit and teachings of the subject matter. The aspects described herein are exemplary only and are not intended to be limiting. Many variations and modifications of the subject matter disclosed herein are possible and are within the scope of the disclosed subject matter. Where numerical ranges or limitations are expressly stated, such express ranges or limitations should be understood to include iterative ranges or limitations of like magnitude falling within the expressly stated ranges or limitations (e.g., from about 1 to about 10 includes, 2, 3, 4,

etc.; greater than 0.10 includes 0.11, 0.12, 0.13, etc.). Use of the term "optionally" with respect to any element of a claim is intended to mean that the subject element is required, or alternatively, is not required. Both alternatives are intended to be within the scope of the claim. Use of broader terms such as comprises, includes, having, etc. should be understood to provide support for narrower terms such as consisting of, consisting essentially of, comprised substantially of, etc.

[0091] Accordingly, the scope of protection is not limited by the description set out above but is only limited by the claims which follow, that scope including all equivalents of the subject matter of the claims. Each and every claim is incorporated into the specification as an aspect of the present disclosure. Thus, the claims are a further description and are an addition to the aspects of the present invention. The discussion of a reference herein is not an admission that it is prior art to the presently disclosed subject matter, especially any reference that may have a publication date after the priority date of this application. The disclosures of all patents, patent applications, and publications cited herein are hereby incorporated by reference, to the extent that they provide exemplary, procedural or other details supplementary to those set forth herein.

CLAIMS

What is claimed is:

1. A polymeric material, comprising:
   a base monomer; and
   a multifunctional biobased molecule, wherein the multifunctional biobased molecule is a glucose derivative.

2. The polymeric material of claim 1, wherein the glucose derivative is a sugar oxidation product.

3. The polymeric material of claim 1, wherein the glucose derivative comprises glucaric acid, gluconic acid, glucuronic acid, galactonic acid and/or galactaric acid with minor component species of n-keto-acids, C2 to C6 diacids, glutamic acid glucodialdose, 2-ketoglucose, or a combination thereof.

4. The polymeric material of claim 1, wherein the multifunctional biobased molecule comprises glucodiamine, gluconamide, glucaramide glucohexadialdose glucaric acid, gluconic acid, 1,4:6,3 glucaric acid dilactone, or a combination thereof.

5. The polymeric material of claim 1, wherein the base monomer forms comprises an amide, an ester, ethylene ,urethane, phenol, or a combination thereof,

6. The polymeric material of claim 1, wherein the multifunctional biobased molecule is present in an amount of from about 1 wt.% to about 50 wt.% based on the total weight of the polymeric material.

7. The polymeric material of claim 1, wherein the polymeric material has a biodegradability that is increased by from about 5% to about 100% when compared to the base polymer.

8. The polymeric material of claim 1, wherein the base monomer comprises a phenol and the multifunctional biobased additive comprises glucodialdose.

9. The polymeric material of claim 1, wherein the base monomer comprises an amide and the multifunctional biobased additive comprises glucodialdose.

10. The polymeric material of claim 1, wherein the base monomer comprises an amide and the multifunctional biobased additive comprises glucaro diamide.

11. The polymeric material of claim 1, wherein the base monomer comprises an pamide and the multifunctional biobased additive comprises glucono amide.

12. The polymeric material of claim 1, wherein the base monomer comprises an amide and the multifunctional biobased additive comprises a mixture of glucaro dimides and glucono amides.

13. The polymeric material of claim 1, wherein the base monomer comprises an amide and the multifunctional biobased additive comprises a mixture of glucodialdose and glucodiamine

14. The polymeric material of claim 1, wherein the base monomer comprises an amide and the multifunctional biobased additive comprises a mixture of glucaric acid and glucodiamine.

15. The polymeric material of claim 1, further comprising erythorbic acid, lactic acid, adipic acid, sorbitol, glycerol, mannitol, lactones thereof, salts thereof, or combinations thereof.

16. A polymeric material, comprising:

a base polymer; and

a polymeric additive comprising glucaric acid, glucodialdose, gluconic acid, erythorbic acid, 2-ketoglucose, lactic acid, adipic acid, sorbitol, glycerol, mannitol, lactones thereof, salts thereof, or a combination thereof;

wherein the additive when contacted with a base polymer forms a modified polymer, wherein the modified polymer has a tensile strength that is increased by from about 10% to about 100% wherein compared to the base polymer.

17. The polymeric material of claim 16, wherein the base polymer comprises a polyester.

18. The polymeric material of claim 16, wherein the base polymer comprises a polylactic acid.

19. The polymeric material of claim 16, wherein the base polymer comprises polyurethane.

20. A hydrogel comprising the polymeric material of claim 1.

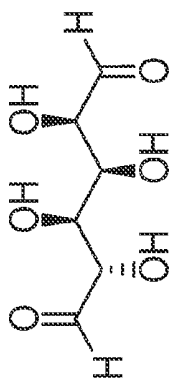


FIG. 1A

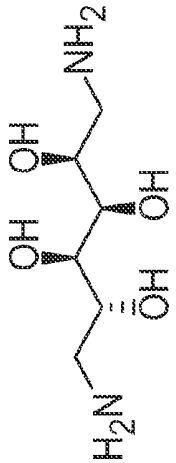


FIG. 1B

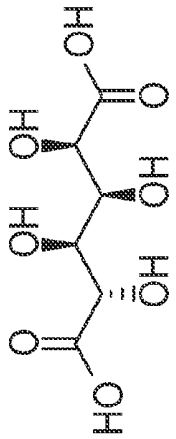


FIG. 1C

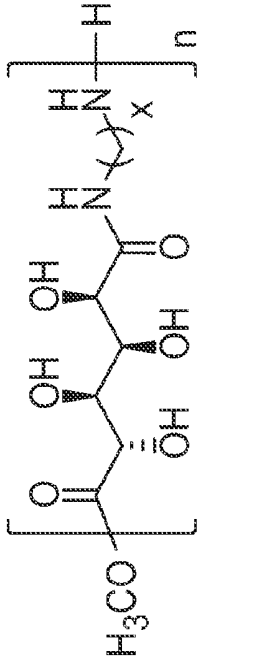


FIG. 1D

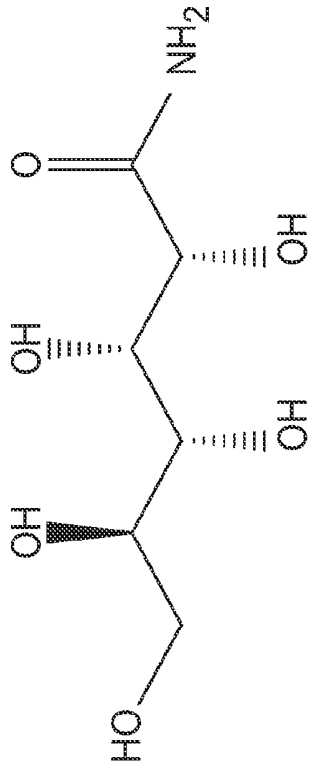


FIG. 1E

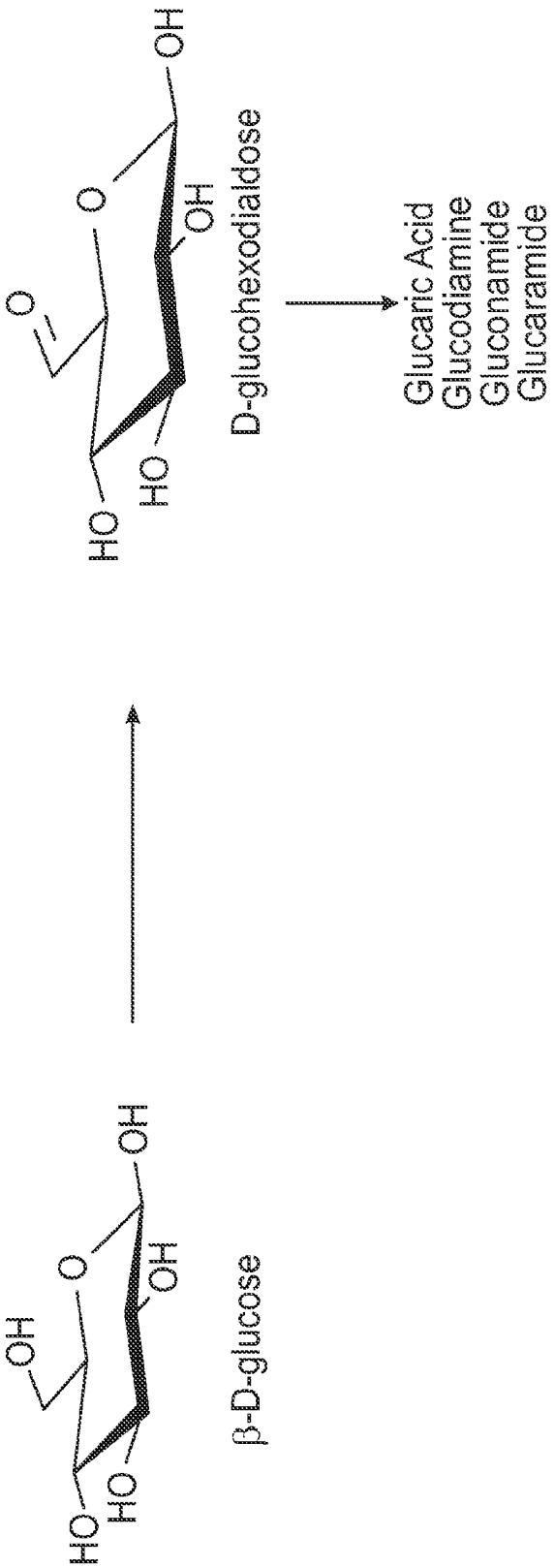

β-D-glucose
D-glucohexodialdose
Glucaric Acid
Glucodiamine
Gluconamide
Glucaramide

FIG. 2

Diamines

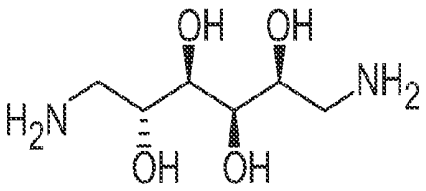


FIG. 3A

OR

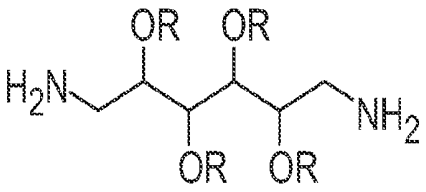


FIG. 3B

OR

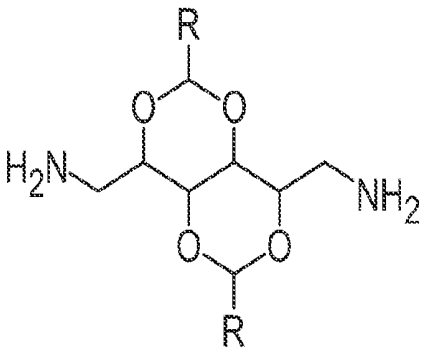


FIG. 3C

OR

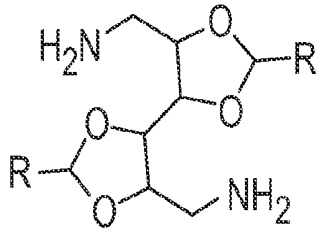


FIG. 3D

Diacids / Di acyl chlorides

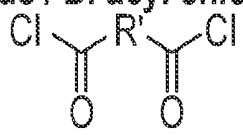


FIG. 3E

OR

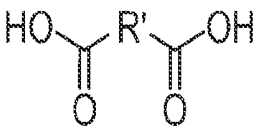


FIG. 3F

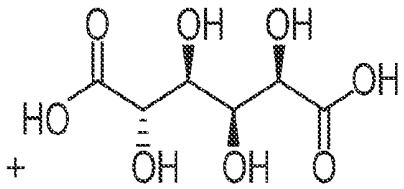


FIG. 3G

Polyamides

OR

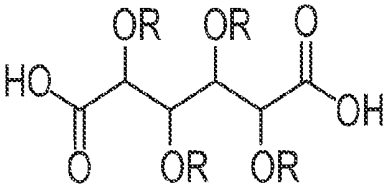


FIG. 3H

OR

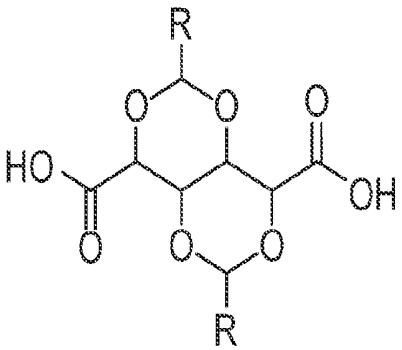


FIG. 3I

OR

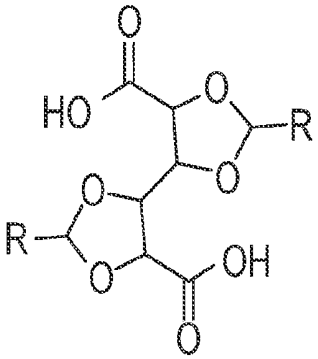


FIG. 3J

Examples:

R = H, Me, Tr, C_xH_{2x+1}, Bn ...

R' = C_2, C_4, C_6 (saturated, unsturated, carbohydrate), aromatics

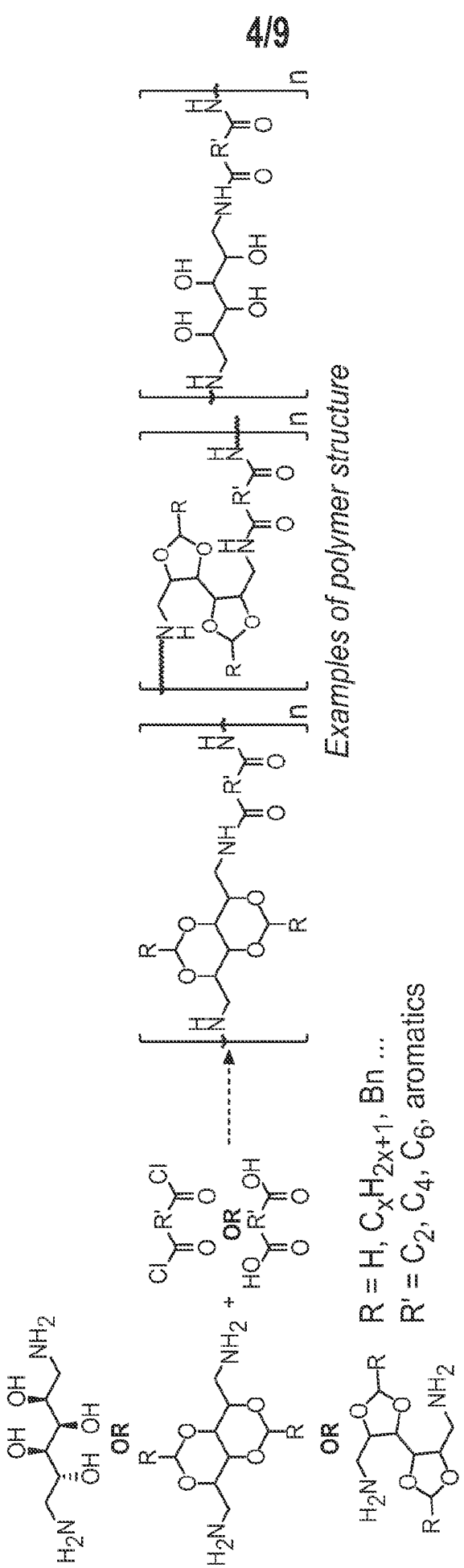

OR
OR
OR
R = H, C_xH_{2x+1}, Bn ...
R' = C_2, C_4, C_6, aromatics
Examples of polymer structure

FIG. 4

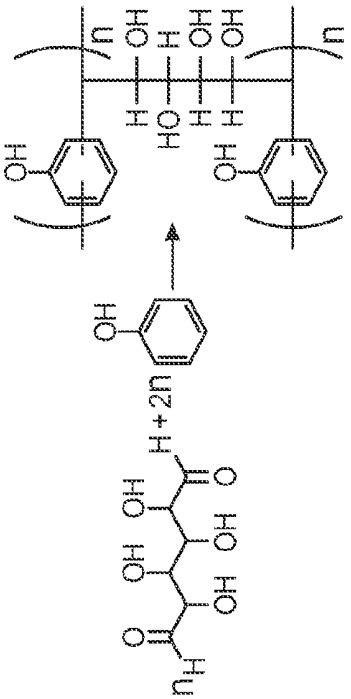


FIG. 5A

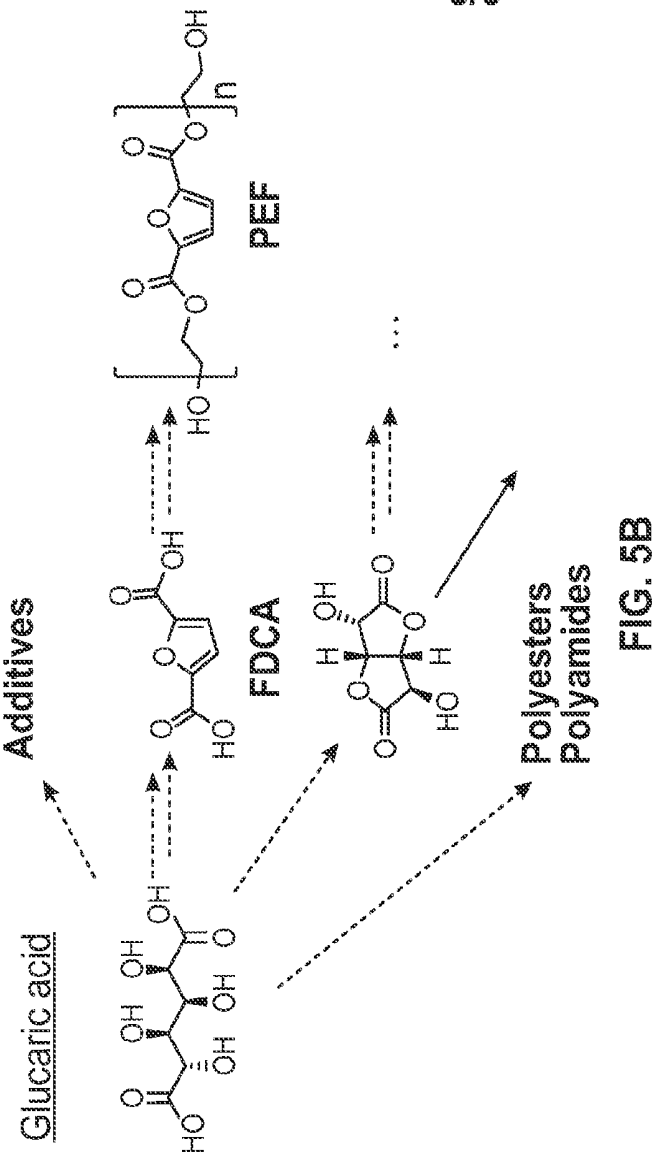
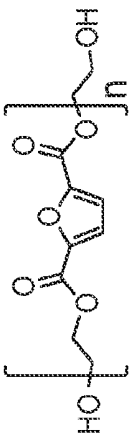
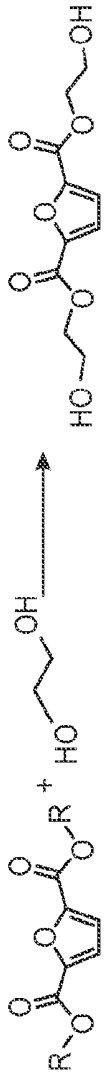


FIG. 5B



PEF



FDCA (R=H)
dmFDCA (R=Me)

FIG. 5C

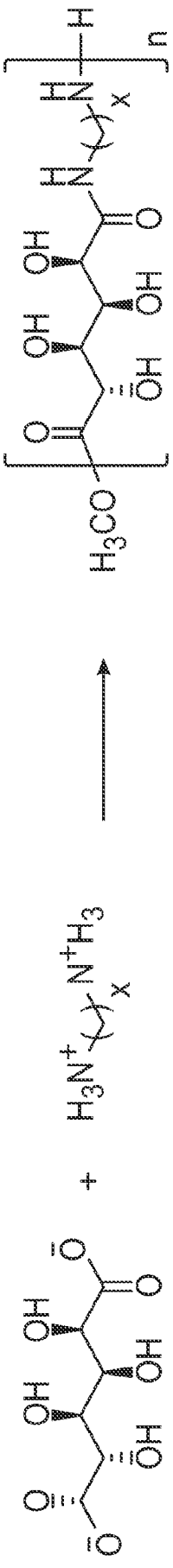
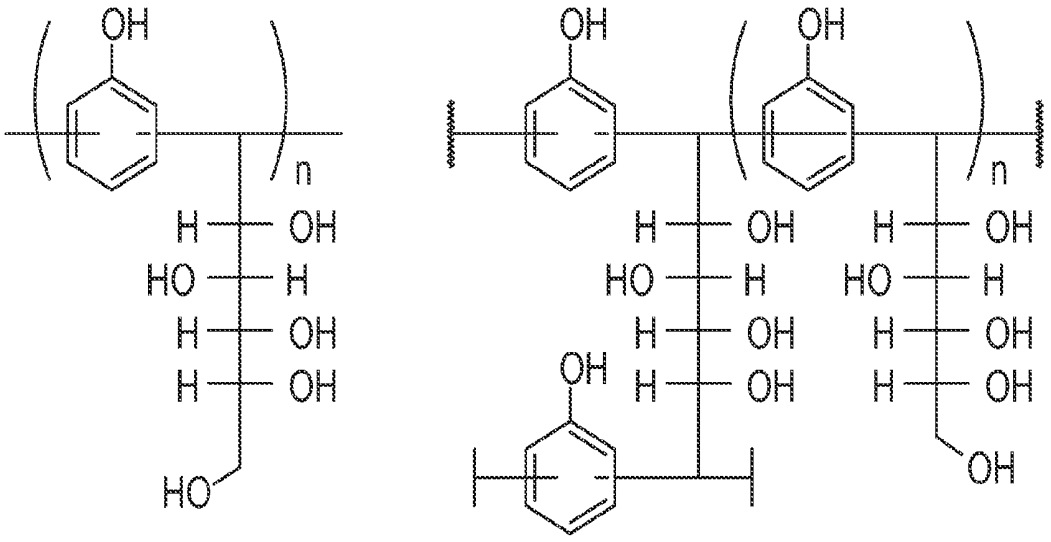


FIG. 5D



P(Glu) P(Glu: GDLA)

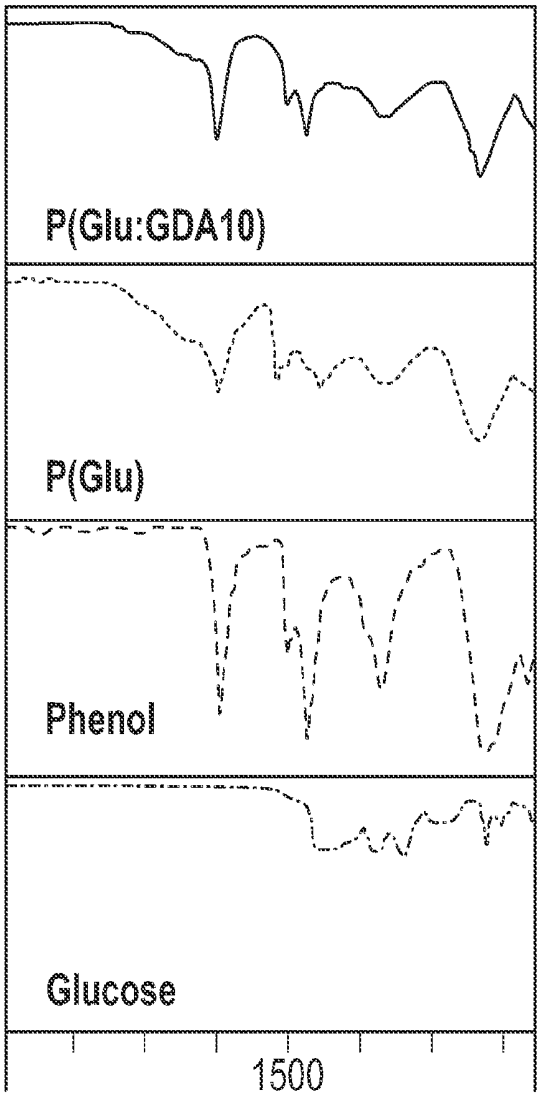


FIG. 6

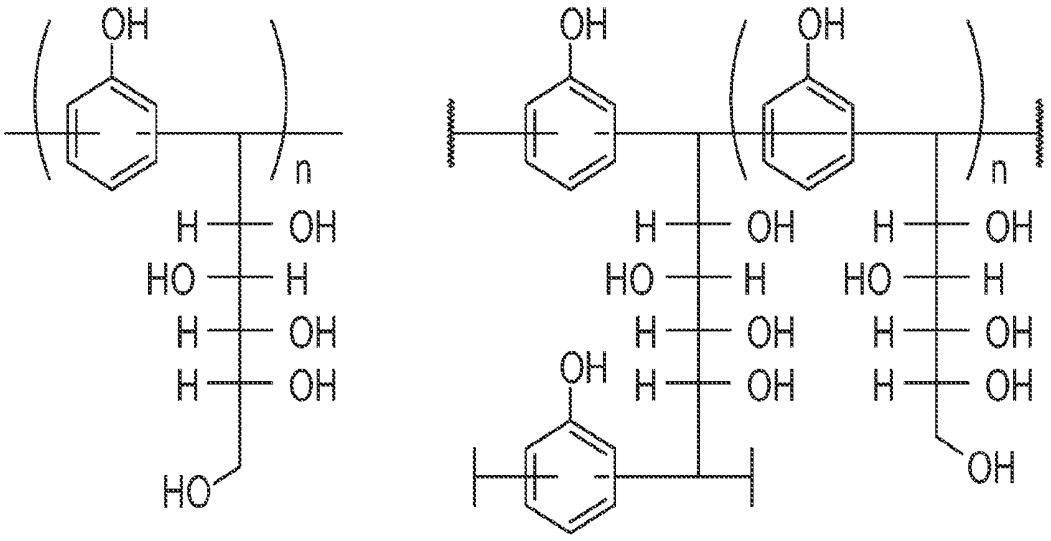

OH
n
H
OH
HO
H
H
OH
H
OH
HO
P(Glu)
OH
OH
n
H
OH
HO
H
H
OH
H
OH
OH
H
OH
HO
H
H
OH
H
OH
OH
P(Glu:GDAX)

FIG. 7

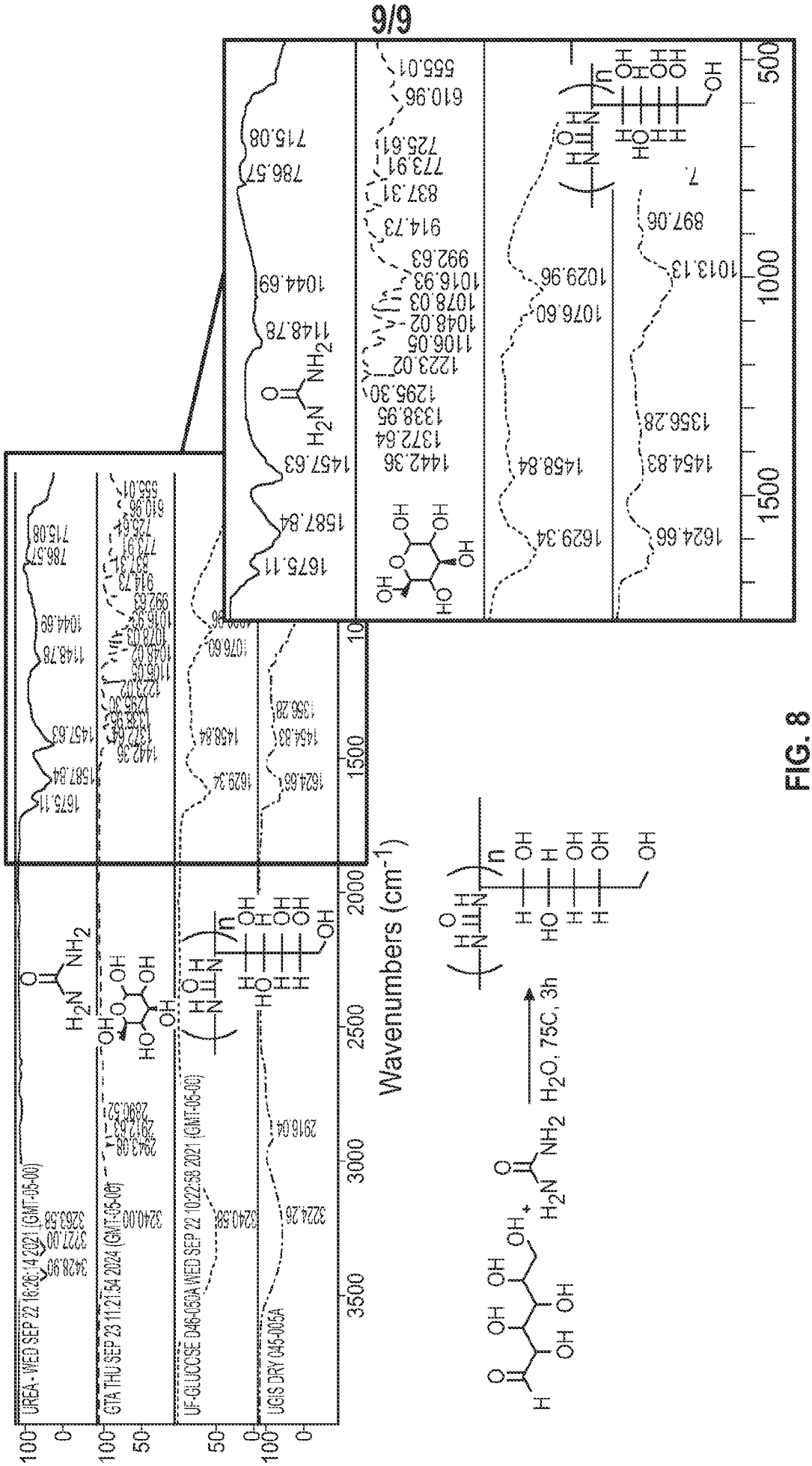

UREA - WED SEP 22 16:26:14 2021 (GMT-05-00)
GTA THU SEP 23 11:21:54 2024 (GMT-05-00)
UF-GLUCOSE D46-050A WED SEP 22 10:22:58 2021 (GMT-05-00)
UGIS DRY D45-005A
Wavenumbers (cm-1)
H2O, 75C, 3h

FIG. 8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2024/054549

A. CLASSIFICATION OF SUBJECT MATTER

IPC: ***C08G 63/06*** (2024.01); ***C08G 69/10*** (2024.01); ***C08G 71/04*** (2024.01); ***C07C 235/10*** (2024.01); ***C07H 1/02*** (2024.01); ***C07H 5/06*** (2024.01)

CPC: ***C08G 63/06; C07C 235/10; C07H 1/02; C07H 5/06; C08G 69/10; C08G 71/04***

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

See Search History Document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

See Search History Document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

See Search History Document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,308,148 A (BOUTIN et al.) 29 December 1981 (29.12.1981) entire document	1-7, 15
X	US 2023/0106704 A1 (THE PROCTER & GAMBLE COMPANY) 06 April 2023 (06.04.2023) entire document	1, 20
X	US 2010/0272940 A1 (SHI et al.) 28 October 2010 (28.10.2010) entire document	16-19
A	WO 2022/261349 A1 (SOLUGEN INC.) 15 December 2022 (15.12.2022) entire document	1-20
A	WO 2023/044168 A1 (SOLUGEN INC.) 23 March 2023 (23.03.2023) entire document	1-20
P, X	WO 2024/227189 A2 (SOLUGEN INC.) 31 October 2024 (31.10.2024) entire document	1-20

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"D" document cited by the applicant in the international application
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
21 December 2024 (21.12.2024)	**03 January 2025 (03.01.2025)**

Name and mailing address of the ISA/US	Authorized officer
COMMISSIONER FOR PATENTS **MAIL STOP PCT, ATTN: ISA/US** **P.O. Box 1450** **Alexandria, VA 22313-1450** **UNITED STATES OF AMERICA**	**TAINA MATOS**
Facsimile No. **571-273-8300**	Telephone No. **571-272-4300**