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(54) Title: ELECTRICALLY-CONDUCTIVE COPOLYESTERCARBONATE-BASED MATERIAL

(57) Abstract: An electrically-conductive material includes a polymeric substrate and a conductive nano structured or micro structured material adhered to at least one surface of the polymeric substrate. The polymeric substrate includes a polymeric block copolyester-carbonate derived from resorcinol or alkylresorcinol isophthalate-terepthalate. The polymeric block copolyestercarbonate has a glass transition temperature of at least 130 degrees Celsius (°C) and a sheet resistance of less than 20 ohms (Ω) per square (sq). Methods for making an electrically-conductive material are also described. The electrically-conductive material may exhibit improved properties, including but not limited to one or more of inherent ultraviolet resistance, transparency, light transmission properties, chemical resistance and/or sheet resistance.

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ELECTRICALLY-CONDUCTIVE COPOLYESTERCARBONATE-BASED MATERIAL

FIELD OF THE DISCLOSURE

[0001] The present disclosure generally relates to electrically conductive materials. More particularly, the disclosure relates to electrically-conductive copolyestercarbonate-based materials having particular performance characteristics.

BACKGROUND OF THE DISCLOSURE

[0002] Conductive substrates in used today are predominantly formed of transparent conductive metal oxides (TCOs), such as indium-tin oxide (ITO), which may be combined with other oxides and then coated with a thin layer of glass or polyethylene terephthalate (PET). Such substrates are not suitable for applications that require enhanced flexibility and impact resistance, however. For such applications, one cost-effective manner to produce flexible electronics is known as the roll-to-roll (R2R) process, which is somewhat analogous to a newspaper printing line.

[0003] A drying step is typically included in the R2R process and is preferably performed at a temperature as high as possible to quickly and effectively remove solvents or dispersion liquids used for inks or other materials that are part of the various layers which make up the so-called flexible electronics "stack." PET has a relatively low glass transition temperature of 78 degrees Celsius (°C), however, which results in limitations in its use in manufacturing applications utilizing the R2R process.

[0004] Moreover, TCOs have limitations in terms of their flexibility. Various new conductive technologies have been developed which outperform TCOs in the R2R manufacturing process. Such conductive technologies include silver nano-wire (AgNW) and silver nano-mesh (AgNM) coatings, which have been applied to PET. In addition to being flexible, substrates including AgNW and AgNM have demonstrated good light transmission properties. The PET substrates currently in use suffer from poor glass transition temperature properties described above, however, limiting their usefulness in some applications.

[0005] These and other shortcomings are addressed by aspects of the present disclosure.

BRIEF DESCRIPTION OF THE FIGURES

[0006] In the drawings, which are not necessarily drawn to scale, like numerals may describe similar components in different views. Like numerals having different letter suffixes may represent different instances of similar components. The drawings illustrate generally, by way of example, but not by way of limitation, various aspects discussed in the present document.

[0007] FIG. 1 is a block diagram illustrating a method for making an electrically-conductive material according to an aspect of the disclosure.

[0008] FIG. 2 is a nanometer-scale image of the surface of a polymeric substrate according to an aspect of the disclosure.

[0009] FIGS. 3A and 3B are graphs of sheet resistance vs. time comparing prior art conductive materials to polymeric materials according to aspects of the present disclosure.

SUMMARY

[0010] Aspects of the disclosure relate to an electrically -conductive material including a polymeric substrate and a conductive nanostructured or microstructured material adhered to at least one surface of the polymeric substrate. The polymeric substrate includes a polymeric block copolyestercarbonate derived from resorcinol or alkylresorcinol isophthalate-terepthalate. The polymeric block copolyestercarbonate has a glass transition temperature of at least 130 degrees Celsius (°C) and a sheet resistance of less than 20 ohms (Ω) per square (sq).

[0011] Further aspects of the disclosure relate to a method for making an electrically-conductive material, the method including: applying a conductive nanostructured or microstructured material onto at least one surface of a polymeric substrate; heating the at least one surface of the polymeric substrate to a temperature that is greater than the glass transition temperature of the polymeric substrate; and applying pressure to the conductive nanostructured or microstructured material and the at least one surface to adhere the conductive nanostructured or microstructured material to the at least one surface. The polymeric substrate has a glass transition temperature of at least 130 °C. The polymeric substrate includes a polymeric block copolyestercarbonate derived from resorcinol or alkylresorcinol isophthalate-terepthalate and has a sheet resistance of less than 20 ohms (Ω) per square (sq).

DETAILED DESCRIPTION

[0012] The present disclosure can be understood more readily by reference to the following detailed description of the disclosure and the Examples included therein. In various aspects, the present disclosure pertains to electrically-conductive material including a polymeric substrate and a conductive nanostructured or microstructured material adhered to at least one surface of the polymeric substrate. The polymeric substrate includes a polymeric block copolyestercarbonate derived from resorcinol or alkylresorcinol isophthalate-terepthalate. The polymeric block copolyestercarbonate has a glass transition temperature of at least 130 degrees Celsius (°C) and a sheet resistance of less than 20 ohms (Ω) per square (sq). In an aspect, the electrically-conductive material exhibits improved properties, including but not limited to one or more of inherent ultraviolet resistance, transparency, light transmission properties, chemical resistance and/or sheet resistance.

[0013] Before the present compounds, compositions, articles, systems, devices, and/or methods are disclosed and described, it is to be understood that they are not limited to specific synthetic methods unless otherwise specified, or to particular reagents unless otherwise specified, as such can, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular aspects only and is not intended to be limiting.

[0014] Various combinations of elements of this disclosure are encompassed by this disclosure, e.g., combinations of elements from dependent claims that depend upon the same independent claim.

[0015] Moreover, it is to be understood that unless otherwise expressly stated, it is in no way intended that any method set forth herein be construed as requiring that its steps be performed in a specific order. Accordingly, where a method claim does not actually recite an order to be followed by its steps or it is not otherwise specifically stated in the claims or descriptions that the steps are to be limited to a specific order, it is no way intended that an order be inferred, in any respect. This holds for any possible non-express basis for interpretation, including: matters of logic with respect to arrangement of steps or operational flow; plain meaning derived from grammatical organization or punctuation; and the number or type of aspects described in the specification.

[0016] All publications mentioned herein are incorporated herein by reference to disclose and describe the methods and/or materials in connection with which the publications are cited.

Definitions

[0017] It is also to be understood that the terminology used herein is for the purpose of describing particular aspects only and is not intended to be limiting. As used in the specification and in the claims, the term "comprising" can include the aspects "consisting of and "consisting essentially of." Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this disclosure belongs. In this specification and in the claims which follow, reference will be made to a number of terms which shall be defined herein.

[0018] As used in the specification and the appended claims, the singular forms "a," "an" and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "a polyestercarbonate" includes mixtures of two or more polyestercarbonate polymers.

[0019] As used herein, the term "combination" is inclusive of blends, mixtures, alloys, reaction products, and the like.

[0020] Ranges can be expressed herein as from one value (first value) to another value (second value). When such a range is expressed, the range includes in some aspects one or both of the first value and the second value. Similarly, when values are expressed as approximations, by use of the antecedent 'about,' it will be understood that the particular value forms another aspect. It will be further understood that the endpoints of each of the ranges are significant both in relation to the other endpoint, and independently of the other endpoint. It is also understood that there are a number of values disclosed herein, and that each value is also herein disclosed as "about" that particular value in addition to the value itself. For example, if the value "10" is disclosed, then "about 10" is also disclosed. It is also understood that each unit between two particular units are also disclosed. For example, if 10 and 15 are disclosed, then 11, 12, 13, and 14 are also disclosed.

[0021] As used herein, the terms "about" and "at or about" mean that the amount or value in question can be the designated value, approximately the designated value, or about the same as the designated value. It is generally understood, as used herein, that it is the nominal value indicated ±10% variation unless otherwise indicated or inferred. The term is intended to convey that similar values promote equivalent results or effects recited in the claims. That is, it is understood that amounts, sizes, formulations, parameters, and other quantities and characteristics are not and need not be exact, but can be approximate and/or larger or smaller, as desired, reflecting tolerances, conversion factors, rounding off, measurement error and the like, and other factors known to those of skill in the art. In general, an amount, size, formulation, parameter or other quantity or characteristic is "about" or "approximate" whether or not expressly stated to be such. It is understood that where "about" is used before a quantitative value, the parameter also includes the specific quantitative value itself, unless specifically stated otherwise.

[0022] Disclosed are the components to be used to prepare the compositions of the disclosure as well as the compositions themselves to be used within the methods disclosed herein. These and other materials are disclosed herein, and it is understood that when combinations, subsets, interactions, groups, etc. of these materials are disclosed that while specific reference of each various individual and collective combinations and permutation of these compounds cannot be explicitly disclosed, each is specifically contemplated and described herein. For example, if a particular compound is disclosed and discussed and a number of modifications that can be made to a number of molecules including the compounds are discussed, specifically contemplated is each and every combination and permutation of the compound and the modifications that are possible unless specifically indicated to the contrary. Thus, if a class of molecules A, B, and C are disclosed as well as a class of molecules D, E, and F and an example of a combination molecule, A-D is disclosed, then even if each is not individually recited each is individually and collectively contemplated meaning combinations, A-E, A-F, B-D, B-E, B-F, C-D, C-E, and C-F are considered disclosed. Likewise, any subset or combination of these is also disclosed. Thus, for example, the sub-group of A-E, B-F, and C-E would be considered disclosed. This concept applies to all aspects of this application including, but not limited to, steps in methods of making and using the compositions of the disclosure. Thus, if there are a variety of additional steps that can be performed it is understood that each of these additional steps can be performed with any specific aspect or combination of aspects of the methods of the disclosure.

[0023] References in the specification and concluding claims to parts by weight of a particular element or component in a composition or article, denotes the weight relationship between the element or component and any other elements or components in the composition or article for which a part by weight is expressed. Thus, in a compound containing 2 parts by weight of component X and 5 parts by weight component Y, X and Y are present at a weight ratio of 2:5, and are present in such ratio regardless of whether additional components are contained in the compound.

[0024] A weight percent of a component, unless specifically stated to the contrary, is based on the total weight of the formulation or composition in which the component is included.

[0025] As used herein the terms "weight percent," "wt%," and "wt. %," which can be used interchangeably, indicate the percent by weight of a given component based on the total weight of the composition, unless otherwise specified. That is, unless otherwise specified, all wt% values are based on the total weight of the composition. It should be understood that the sum of wt% values for all components in a disclosed composition or formulation are equal to 100.

[0026] Unless otherwise stated to the contrary herein, all test standards are the most recent standard in effect at the time of filing this application.

[0027] "Adhere" or "adhered" refers to the attachment or adhesion between the conductive nanostructured or microstructured material and the surface of the polymeric substrate. In certain aspects, and after employing the process of the present disclosure, the conductive nanostructured or microstructured material is sufficiently attached to the surface of the substrate such that it is conductive after being subjected to the Scotch tape test or the bending test or both. The scotch tap test consists of firmly pressing by hand scotch tape to the produced surface and then peeling off said Scotch tape. The bending test consists of bending the produced electrically-conductive material around a rod having a radius of about 0.625 millimeters (mm).

[0028] "Nanostructure" refers to an object or material in which at least one dimension of the object or material is equal to or less than 100 nanometers (nm) (e.g., one dimension is 1 to 100 nm in size). In a particular aspect, the nanostructure includes at least two dimensions that are equal to or less than 100 nm (e.g., a first dimension is 1 to 100 nm in size and a second dimension is 1 to 100 nm in size). In another aspect, the nanostructure includes three dimensions that are equal to or less than 100 nm (e.g., a first dimension is 1 to 100 nm in size, a second dimension is 1 to 100 nm in size, and a third dimension is 1 to 100 nm in size). The shape of the nanostructure can be of a wire, a particle, a sphere, a rod, a tetrapod, a hyperbranched structure, or mixtures thereof.

[0029] "Microstructure" refers to an object or material in which at least one dimension of the object or material is equal to or less than 1000 microns and greater than 100 nm (e.g., one dimension is greater than 100 nm and less than 1000 microns in size). In a particular aspect, the microstructure includes at least two dimensions that are equal to or less than 1000 microns and greater than 100 nm (e.g., a first dimension is greater than 100 nm and less than 1000 microns in size and a second dimension is greater than 100 nm and less than 1000 microns in size). In another aspect, the microstructure includes three dimensions that are equal to or less than 1000 microns and greater than 100 nm (e.g., a first dimension is greater than 100 nm and less than 1000 microns in size, a second dimension is greater than 100 nm and less than 1000 microns in size, and a third dimension is greater than 100 nm and less than 1000 microns in size). The shape of the microstructure can be of a wire, a particle, a sphere, a rod, a tetra-pod, a hyperbranched structure, or mixtures thereof.

[0030] The term "substantially" is defined as being largely but not necessarily wholly what is specified (and include wholly what is specified) as understood by one of ordinary skill in the art. In any disclosed aspect, the term "substantially" may be substituted with "within [a percentage] of what is specified, where the percentage includes 0.1, 1, 5, and 10 percent.

[0031] Each of the materials disclosed herein are either commercially available and/or the methods for the production thereof are known to those of skill in the art.

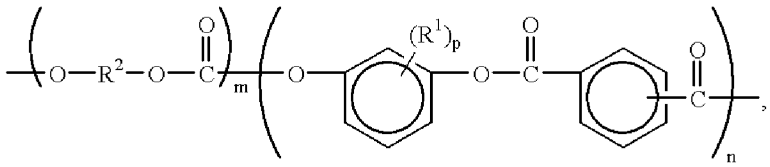
[0032] It is understood that the compositions disclosed herein have certain functions. Disclosed herein are certain structural requirements for performing the disclosed functions and it is understood that there are a variety of structures that can perform the same function that are related to the disclosed structures, and that these structures will typically achieve the same result.

Electrically Conductive Materials

[0033] Aspects of the disclosure relate to an electrically-conductive material including a polymeric substrate and a conductive nanostructured or microstructured material adhered to at least one surface of the polymeric substrate. The polymeric substrate includes a polymeric block copolyestercarbonate derived from resorcinol or alkylresorcinol isophthalate-terepthalate. In certain aspects the polymeric block copolyestercarbonate has a glass transition temperature of at least 130 degrees Celsius (°C) and has a sheet resistance of less than 20 ohms (Ω) per square (sq).

[0034] In some aspects the polymeric block copolyestercarbonate may be any of those copolyestercarbonates described in U.S. Patent No. 6,583,256, the disclosure of which is incorporated herein by this reference in its entirety, provided that the polymeric block copolyestercarbonate has a glass transition temperature of at least 130 degrees °C and has a sheet resistance of less than 20 Ω/sq as described herein. In particular aspects, the polymeric block copolyestercarbonate comprises organic carbonate blocks alternating with arylate blocks. Suitable block copolyestercarbonates include polymers comprising structural units of Formula I:

(I)



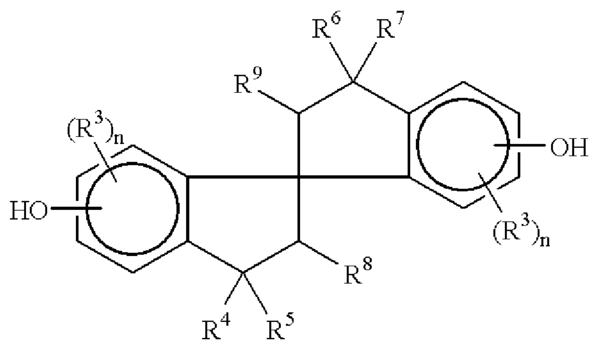
wherein each R^1 is independently halogen or C_{1-12} alkyl, p is 0-3, each R^2 is independently a divalent organic radical, m is at least 1 and n is at least about 4. In some aspects n is at least about 10, or at least about 20, or about 30-150. In certain aspects m is at least about 3, or at least about 10, or about 20-200. In particular aspects m is between about 20 and 50. Within the context of the disclosure "alternating carbonate and arylate blocks" means that the copolyestercarbonates comprise at least one carbonate block and at least one arylate block.

[0035] The arylate blocks contain structural units comprising 1,3-dihydroxybenzene moieties which may be unsubstituted or substituted. Alkyl substituents, if present, may be straight-chain or branched alkyl groups, and are most often located in the ortho position to both oxygen atoms although other ring locations are contemplated. Suitable C_{1-12} alkyl groups include methyl, ethyl, n-propyl, isopropyl, butyl, iso-butyl, t-butyl, nonyl, decyl, and aryl-substituted alkyl, including benzyl, with methyl being particularly preferred in some aspects. Suitable halogen substituents are bromo, chloro, and fluoro. 1,3-Dihydroxybenzene moieties containing a mixture of alkyl and halogen substituents are also suitable. The value for p may be 0-3, or 0-2, or even 0-1. One particular 1,3-dihydroxybenzene moiety is 2-methylresorcinol. A certain 1,3-dihydroxybenzene moiety is unsubstituted resorcinol in which p is zero. Polymers containing mixtures of 1,3-dihydroxybenzene moieties, such as a mixture of unsubstituted resorcinol with 2-methylresorcinol are also contemplated.

[0036] In the arylate structural units the 1,3-dihydroxybenzene moieties are bound to aromatic dicarboxylic acid moieties which may be monocyclic moieties, such as isophthalate or terephthalate or their chlorine-substituted derivatives; or polycyclic moieties, such as biphenyl dicarboxylate, diphenylether dicarboxylate, diphenylsulfone dicarboxylate, diphenylketone dicarboxylate, diphenylsulfide dicarboxylate, or naphthalenedicarboxylate, and in some aspects preferably naphthalene-2,6-dicarboxylate; or mixtures of monocyclic and/or polycyclic aromatic dicarboxylates. In some aspects the aromatic dicarboxylic acid moieties are isophthalate and/or terephthalate. Either or both of said moieties may be present. For the most part, both are present in a molar ratio of isophthalate to terephthalate in the range of about 0.25-4.0: 1. When the isophthalate to terephthalate ratio is greater than about 4.0: 1, then unacceptable levels of cyclic oligomer may form. When the isophthalate to terephthalate ratio is less than about 0.25: 1, then unacceptable levels of insoluble polymer may form. Thus in some aspects the molar ratio of isophthalate to terephthalate is about 0.4-2.5: 1, or from about 0.67-1.5:1.

[0037] In the carbonate blocks, each R^2 is independently an organic radical derived from a dihydroxy compound. For the most part, at least about 60 percent of the total number of R^2 groups in the polymer are aromatic organic radicals and the balance thereof are aliphatic, alicyclic, or aromatic radicals. Suitable R^2 radicals include m-phenylene, p-phenylene, 4,4'-biphenylene, 4,4'-bi(3,5-dimethyl)-phenylene, 2,2-bis(4-phenylene)propane and similar radicals such as those which correspond to the dihydroxy-substituted aromatic hydrocarbons disclosed by name or formula (generic or specific) in U.S. Patent No. 4,217,438, the disclosure of which is incorporated herein by this reference in its entirety. Included among suitable dihydroxy-substituted aromatic hydrocarbons are the 2,2,2',2'-tetrahydro-l,l'-spirobi[lH-indene]diols having Formula II:

(II)



wherein each R^3 is independently selected from monovalent hydrocarbon radicals and halogen radicals; each R^4, R^5, R^6, and R^7 is independently C_{1-6} alkyl; each R^8 and R^9 is independently **H** or C_{1-6} alkyl; and each n is independently selected from positive integers having a value of from 0 to 3 inclusive. A suitable 2,2,2',2'-tetrahydro-l ,1'-spirobi[lH-indene]-diol is 2,2,2',2'-tetrahydro-3,3,3',3'-tetramethyl-l ,1'-spirobi[lH-indene]-6,6'-diol.

[0038] In particular aspects, each R^2 is an aromatic organic radical, and even more particularly a radical of Formula III:

$$—A^1—Y—A^2—, \qquad \text{(III)}$$

wherein each A^1 and A^2 is a monocyclic divalent aryl radical and Y is a bridging radical in which one or two carbon atoms separate A^1 and A^2. The free valence bonds in Formula III are usually in the meta or para positions of A^1 and A^2 in relation to Y. Compounds in which R^2 has Formula III are bisphenols, and for the sake of brevity the term "bisphenol" is sometimes used herein to designate the dihydroxy-substituted aromatic hydrocarbons; it should be understood, however, that non-bisphenol compounds of this type may also be employed as appropriate.

[0039] In Formula III, A^1 and A^2 typically represent unsubstituted phenylene or substituted derivatives thereof, illustrative substituents (one or more) being alkyl, alkenyl, and halogen (particularly bromine). Unsubstituted phenylene radicals are preferred in some aspects. Both A^1 and A^2 may be p-phenylene, although both may be o- or m-phenylene or one o- or m-phenylene and the other p-phenylene.

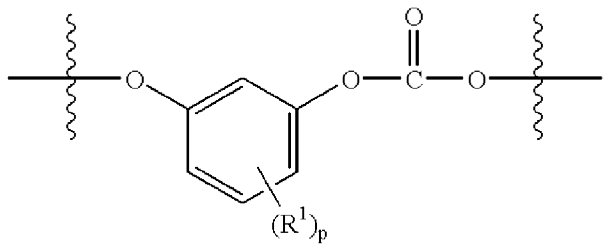
[0040] The bridging radical, Y, is one in which one or two atoms, separate A^1 from A^2. One suitable aspect is one in which one atom separates A^1 from A^2. Illustrative radicals of this type are -C=0, -0-, -S-, -SO- or -SO2-, methylene, cyclohexylmethylene, 2-[2.2.1]-bicycloheptyl methylene, ethylene, isopropylidene, neopentylidene, cyclohexylidene, cyclopentadecylidene, cyclododecylidene, and adamantylidene.

[0041] Gem-alkylene radicals are often suitable. Also included, however, are unsaturated radicals. For reasons of availability and particular suitability for the purposes of the present disclosure, a particular bisphenol is 2,2-bis(4-hydroxy-phenyl)propane (hereinafter referred to as bisphenol A or BPA), in which Y is isopropylidene and A^1 and A^2 are each p-phenylene.

[0042] Depending upon whether or not any unreacted 1,3-dihydroxybenzene moiety is present in the reaction mixture as described hereinafter, R^2 in the carbonate blocks may consist of or at least partially comprise a radical derived from a 1,3-dihydroxybenzene moiety. Therefore, in one aspect the copolyestercarbonates comprise carbonate blocks with R^2 radicals derived from a dihydroxy compound identical to at least one 1,3-dihydroxybenzene moiety in the polyarylate blocks. In another aspect the copolyestercarbonates comprise carbonate blocks with R^2 radicals derived from a dihydroxy compound different from any 1,3-dihydroxybenzene moiety in the polyarylate blocks. In yet another aspect the copolyestercarbonates comprise carbonate blocks containing a mixture of R^2 radicals derived from dihydroxy compounds at least one of which is the same as and at least one of which is different from any 1,3-dihydroxybenzene moiety in the polyarylate blocks. When a mixture of R^2 radicals derived from dihydroxy compounds is present, then the molar ratio of dihydroxy compounds identical to those present in the polyarylate blocks to those dihydroxy compounds different from those present in the polyarylate blocks is typically about 1:999 to 999: 1. In particular aspects the copolyestercarbonates comprise carbonate blocks containing a mixture of R^2 radicals derived from at least two of unsubstituted resorcinol, a substituted resorcinol, and bisphenol A.

[0043] Diblock, triblock, and multiblock copolyestercarbonates are encompassed in aspects of the present disclosure. The chemical linkages between blocks comprising arylate chain members and blocks comprising organic carbonate chain members typically comprise a carbonate linkage between a diphenol residue of an arylate moiety and a - C=0) -O- moiety of an organic carbonate moiety, although other types of linkages such as ester and/or anhydride are also possible. A typical carbonate linkage between said blocks is shown in Formula IV, wherein R^1 and p are as previously defined:

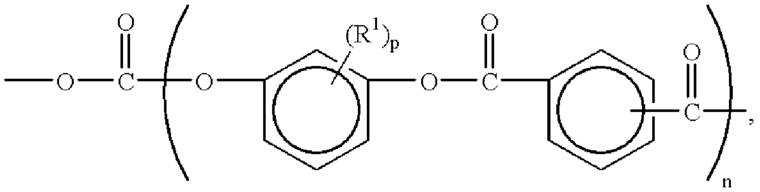
(IV)



[0044] In one aspect the copolyestercarbonate is substantially comprised of a diblock copolymer with a carbonate linkage between an arylate block and an organic carbonate block. In another aspect the copolyestercarbonate is substantially comprised of a triblock carbonate-ester-carbonate copolymer with carbonate linkages between the arylate block and organic carbonate end-blocks. Copolyestercarbonates with at least one carbonate linkage between an arylate block and an organic carbonate block are typically prepared from 1,3-dihydroxybenzene arylate-containing oligomers containing at least one and in some aspects preferably two hydroxy-terminal sites (hereinafter sometimes referred to as hydroxy-terminated polyester intermediate).

[0045] In another aspect the copolyestercarbonate comprises arylate blocks linked by carbonate linkages as shown in Formula V:

(V)



wherein R^1, p, and n are as previously defined, and the arylate structural units are as described for Formula I. Copolyestercarbonates comprising Formula V may arise from reaction of hydroxy-terminated polyester intermediate with a carbonate precursor in the substantial absence of any dihydroxy compound different from the hydroxy-terminated polyester intermediate.

[0046] In the copolyestercarbonates according to aspects of the present disclosure the distribution of the blocks may be such as to provide a copolymer having any desired weight proportion of arylate blocks in relation to carbonate blocks. In general, copolymers containing about 10-99% by weight arylate blocks are preferred.

[0047] In further aspects the polymeric block copolyestercarbonate may be any of those copolyestercarbonates described in U.S. Patent No. 6,143,839, the disclosure of which is incorporated herein by this reference in its entirety, provided that the polymeric block copolyestercarbonate has a glass transition temperature of at least 130 °C and has a sheet resistance of less than 20 Ω/sq as described herein.

[0048] In some aspects the polymeric block copolyestercarbonate has a glass transition temperature of at least 133 °C, or at least 135 °C. In a particular aspect the polymeric block copolyestercarbonate has a glass transition temperature of about 137 °C.

[0049] One particular polymeric block copolyestercarbonate suitable for use in aspects of the disclosure is Lexan® SLX2531T, available from SABIC.

[0050] In some aspects the polymeric block copolyestercarbonate is inherently ultraviolet resistant. In other words, the polymeric block copolyestercarbonate includes in its structure a moiety that blocks ultraviolet radiation and protects the polymer from embrittlement, cracking and other forms of degradation common to polymers when exposed to ultraviolet radiation.

[0051] In certain aspects the electrically-conductive material and/or the polymeric block copolyestercarbonate is transparent. The transparency or translucency of a given object or medium (e.g., electrically-conductive material, polymeric substrate, conductive nanostructured material, conductive microstructured material, etc.) can be determined by measuring the total transmittance of incident light through the object/medium. The reflectivity, translucency, or transparency of an electrically-conductive material produced by the process of the present disclosure can be affected by the amount of conductive nanostructured or microstructured material applied on the substrate's surface. By way of example, the total transmittance of incident light through the produced conductive material can be 0%, 10%, 20%, 30%, 40%, 50%, 60% 70%, 80%, 90%, or more, and this can be adjusted or tuned as desired based on the amount of conductive nanostructured or microstructured material used in the process of the present disclosure. Further, and in instances where the substrate is transparent, additional conductive nanostructured or microstructured material may be used to create a sufficient reflectivity when compared with substrates that are translucent or that are opaque.

[0052] In particular aspects transparency may be described in terms of the amount of light in the visible spectrum of light that is transmitted through the polymeric block copolyestercarbonate, where the visible spectrum of light is generally considered the wavelength range of about 400 to about 700 nanometers (nm). Thus, in some aspects the electrically-conductive material and/or the polymeric block copolyestercarbonate has a light transmission of greater than 80% at a wavelength of 400 to 700 nm. In further aspects the electrically-conductive material and/or the polymeric block copolyestercarbonate has a light transmission of greater than 85% at a wavelength of 400 to 700 nm, or the electrically-conductive material and/or the polymeric block copolyestercarbonate has a light transmission of greater than 90% at a wavelength of 400 to 700 nm.

[0053] In further aspects the electrically-conductive material and/or polymeric block copolyestercarbonate has good chemical resistance properties. Chemical resistance may include one or more of resistance to grease, oil, acidic compounds (including weak and/or dilute acidic compounds), aromatic compounds, alcohols and alkali compounds. The Lexan® SLX253 IT polymer described herein has good resistance to grease, oil, weak/dilute acidic compounds and aromatic compounds and moderate resistance to alcohols and alkali compounds.

[0054] As noted, an electrically-conductive material according to aspects of the disclosure includes a polymeric substrate and a conductive nanostructured or microstructured material adhered to at least one surface of the polymeric substrate. In some aspects the conductive nanostructured or microstructured material includes silver, gold, copper, nickel, gold-plated silver and combinations thereof. In a particular aspect the conductive nanostructured or microstructured material includes silver.

[0055] The conductive nanostructured or microstructured material may be in any suitable form. In particular aspects the conductive nanostructured or microstructured material is in the form of metal nanowires and/or other conductive particles having high aspect ratios (e.g., higher than 10). Non-limiting examples of non-metallic nanowires suitable for aspects of the disclosure include carbon nanotubes (CNTs), metal oxide nanowires, conductive polymer fibers and combinations thereof. In a particular aspect the conductive nanostructured or microstructured material is in the form of nanowires.

[0056] "Conductive nanostructured material" may refer to a network material/layer that comprises nanostructures that is capable of conducting electricity. "Conductive microstructured material" refers to a network material/layer that comprises microstructures that is capable of conducting electricity. Since conductivity is achieved by electrical charge percolating from one nanostructure/microstructure to another, a sufficient amount of nano/micro structures should be present in the conductive layer to reach an electrical percolation threshold and become conductive. The surface conductivity of the conductive nanostructure/microstructure layer is inversely proportional to its surface resistivity, sometimes referred to as sheet resistance, which can be measured by known methods in the art. Further, although the term "conductive nanostructured or microstructured material" is used herein, it will be recognized that the use of nanostructured materials and microstructured materials is not mutually exclusive, and that electrically-conductive materials according to aspects of the disclosure may include both nanostructured materials and microstructured materials.

[0057] In certain aspects the conductive nanostructured or microstructured material is adhered to at least one surface of the polymeric substrate by spray coating it onto the polymeric substrate in accordance with the methods described herein. The at least one surface of the electrically-conductive material may be a substantially smooth surface in some aspects. In some aspects "smooth" means that the surface has surface height variations of less than about 500 nm. In further aspects "smooth" means that the surface has surface height variations of less than about 400 nm, or that the surface has surface height variations of less than about 300 nm, or that the surface has surface height variations of less than about 200 nm, or that the surface has surface height variations of less than about 100 nm, or that the surface has surface height variations of less than about 50 nm. In particular aspects "smooth" means that the surface has surface height variations ranging from about 5 nm to about 50 nm.

Methods for Making an Electrically-Conductive Material

[0058] Aspects of the disclosure further related to methods for making an electrically-conductive material and with reference to FIG. 1 include: applying a conductive nanostructured or microstructured material onto at least one surface of a polymeric substrate, the polymeric substrate having a glass transition temperature of at least 130 °C; heating the at least one surface of the polymeric substrate to a temperature that is greater than the glass transition temperature of the polymeric substrate; and applying pressure to the conductive nanostructured or microstructured material and the at least one surface to adhere the conductive nanostructured or microstructured material to the at least one surface. The polymeric substrate comprises a polymeric block copolyestercarbonate derived from resorcinol or alkylresorcinol isophthalate-terepthalate and has a sheet resistance of less than 20 Ω/sq.

[0059] Specific methods of making the electrically-conductive material include those described in U.S. Patent Publication No. 2015/0037517 ("517 Publication"), published February 5, 2015, the disclosure of which is incorporated herein by this reference in its entirety. With specific reference to FIG. 1, one aspect of the method 100 includes, at step 110, applying a conductive nanostructured or microstructured material onto at least one surface of a polymeric substrate. In some aspects the conductive nanostructured or microstructured material includes silver, gold, copper, nickel, gold-plated silver and combinations thereof. In a particular aspect the conductive nanostructured or microstructured material includes silver.

[0060] The conductive nanostructured or microstructured material may be in any suitable form. In particular aspects the conductive nanostructured or microstructured material is in the form of metal nanowires and/or other conductive particles having high aspect ratios (e.g., higher than 10). Non-limiting examples of non-metallic nanowires suitable for aspects of the disclosure include carbon nanotubes (CNTs), metal oxide nanowires, conductive polymer fibers and combinations thereof. In a particular aspect the conductive nanostructured or microstructured material is in the form of nanowires.

[0061] The conductive nanostructured or microstructured material may be applied to the at least one surface by any suitable method, including but not limited to spray coating, ultrasonic spray coating, roll-to-roll coating, ink jet printing, screen printing, drop casting, spin coating, dip coating, Mayer rod coating, gravure coating, slot die coating, doctor blade coating or a combination thereof. In a particular aspect, the step of applying the conductive nanostructured or microstructured material comprises spray coating the conductive nanostructured or microstructured material onto the at least one surface.

[0062] Aspects of the method further include, at step 120, heating the at least one surface of the polymeric substrate to a temperature that is greater than the glass transition temperature of the polymeric substrate. In some aspects the polymeric block copolyestercarbonate has a glass transition temperature of at least 130 °C. In further aspects the polymeric block copolyestercarbonate has a glass transition temperature of at least 133

°C, or at least 135 °C. In a particular aspect the polymeric block copolyestercarbonate has a glass transition temperature of about 137 °C.

[0063] The method may further include, at step 130, applying pressure to the conductive nanostructured or microstructured material and the at least one surface to adhere the conductive nanostructured or microstructured material to the at least one surface. Pressure can be applied to the conductive nanostructured or microstructured material and the at least one surface by any suitable pressure source, including but not limited to (as explained in the 517 Publication), a roller such as a metallic roller, a ceramic roller, a plastic roller or a rubber roller. Further, the pressure and speed applied by the roller (if used) can be sufficient to cause the conductive nanostructured or microstructured material to adhere to the at least one surface of the polymeric substrate. Purely exemplary pressures range from, e.g., 25 to 300 pounds per square inch (psi) and speeds range from, e.g., 0.1 centimeters per second (cm/s) to 10 cm/s.

[0064] In one aspect, the step of applying pressure to the conductive nanostructured or microstructured material and the at least one surface causes the at least one surface to be substantially smooth (as that term is described herein).

[0065] The polymeric block copolyestercarbonate comprises any one or more of those materials described herein. Further, the polymeric block copolyestercarbonate and may have any of the properties described above, including but not limited to one or more of inherent ultraviolet resistance, transparency, light transmission properties, chemical resistance and/or sheet resistance.

[0066] Various combinations of elements of this disclosure are encompassed by this disclosure, e.g., combinations of elements from dependent claims that depend upon the same independent claim.

Aspects of the Disclosure

[0067] In various aspects, the present disclosure pertains to and includes at least the following aspects.

[0068] Aspect 1: An electrically-conductive material comprising, consisting of or consisting essentially of: a polymeric substrate and a conductive nanostructured or microstructured material adhered to at least one surface of the polymeric substrate, wherein

the polymeric substrate comprises a polymeric block copolyestercarbonate derived from resorcinol or alkylresorcinol isophthalate-terepthalate,

the polymeric block copolyestercarbonate has a glass transition temperature of at least 130 degrees Celsius (°C), and the polymeric block copolyestercarbonate has a sheet resistance of less than 20 ohms (Ω) per square (sq).

[0069] Aspect 2: The electrically-conductive material according to Aspect 1, wherein the polymeric block copolyestercarbonate is inherently ultraviolet resistant.

[0070] Aspect 3: The electrically-conductive material according to Aspect 1 or 2, wherein the electrically-conductive material is transparent.

[0071] Aspect 4: The electrically-conductive material according to any of Aspects 1 to 3, wherein the electrically-conductive material has a light transmission of greater than 80% at a wavelength of 400 to 700 nanometers (nm).

[0072] Aspect 5: The electrically-conductive material according to any of Aspects 1 to 4, wherein the polymeric block copolyestercarbonate has good chemical resistance properties.

[0073] Aspect 6: The electrically-conductive material according to any of Aspects 1 to 5, wherein the conductive nanostructured or microstructured material comprises silver, gold, copper, nickel, gold-plated silver and combinations thereof.

[0074] Aspect 7: The electrically-conductive material according to Aspect 6, wherein the conductive nanostructured or microstructured material comprises silver.

[0075] Aspect 8: The electrically-conductive material according to any of Aspects 1 to 7, wherein the polymeric block copolyestercarbonate has a glass transition temperature of about 137 °C.

[0076] Aspect 9: The electrically-conductive material according to any of Aspects 1 to 8, wherein the conductive nanostructured or microstructured material is spray coated onto the polymeric substrate.

[0077] Aspect 10: The electrically-conductive material according to any of Aspects 1 to 9, wherein the at least one surface is a substantially smooth surface.

[0078] Aspect 11: A method for making an electrically-conductive material comprising, consisting of, or consisting essentially of:

applying a conductive nanostructured or microstructured material onto at least one surface of a polymeric substrate, the polymeric substrate having a glass transition temperature of at least 130 °C;

heating the at least one surface of the polymeric substrate to a temperature that is greater than the glass transition temperature of the polymeric substrate; and applying pressure to the conductive nanostructured or microstructured material and the at least one surface to adhere the conductive nanostructured or microstructured material to the at least one surface,

wherein the polymeric substrate comprises a polymeric block copolyestercarbonate derived from resorcinol or alkylresorcinol isophthalate-terepthalate and has a sheet resistance of less than 20 ohms **(Ω)** per square (sq).

[0079] Aspect 12: The method according to Aspect 11, wherein the step of applying the conductive nanostructured or microstructured material comprises spray coating, ultrasonic spray coating, roll-to-roll coating, ink jet printing, screen printing, drop casting, spin coating, dip coating, Mayer rod coating, gravure coating, slot die coating, or doctor blade coating the conductive nanostructured or microstructured material onto the at least one surface.

[0080] Aspect 13: The method according to Aspect 12, wherein the step of applying the conductive nanostructured or microstructured material comprises spray coating the conductive nanostructured or microstructured material onto the at least one surface.

[0081] Aspect 14: The method according to any of Aspects 11 to 13, wherein the polymeric block copolyestercarbonate is inherently ultraviolet resistant.

[0082] Aspect 15: The method according to any of Aspects 11 to 14, wherein the electrically-conductive material is transparent.

[0083] Aspect 16: The method according to any of Aspects 11 to 15, wherein the electrically-conductive material has a light transmission of greater than 80% at a wavelength of 400 to 700 nanometers (nm).

[0084] Aspect 17: The method according to any of Aspects 11 to 16, wherein the polymeric block copolyestercarbonate has good chemical resistance properties.

[0085] Aspect 18: The method according to any of Aspects 11 to 17, wherein the conductive nanostructured or microstructured material comprises silver, gold, copper, nickel, gold-plated silver and combinations thereof.

[0086] Aspect 19: The method according to Aspect 18, wherein the conductive nanostructured or microstructured material comprises silver.

[0087] Aspect 20: The method according to any of Aspects 11 to 19, wherein the step of applying pressure to the conductive nanostructured or microstructured material and the at least one surface causes the at least one surface to be substantially smooth.

EXAMPLES

[0088] The following examples are put forth so as to provide those of ordinary skill in the art with a complete disclosure and description of how the compounds, compositions, articles, devices and/or methods claimed herein are made and evaluated, and are intended to be purely exemplary and are not intended to limit the disclosure. Efforts have been made to ensure accuracy with respect to numbers (e.g., amounts, temperature, etc.), but some errors and deviations should be accounted for. Unless indicated otherwise, parts are parts by weight, temperature is in °C or is at ambient temperature, and pressure is at or near atmospheric. Unless indicated otherwise, percentages referring to composition are in terms ofwt%.

[0089] There are numerous variations and combinations of reaction conditions, e.g., component concentrations, desired solvents, solvent mixtures, temperatures, pressures and other reaction ranges and conditions that can be used to optimize the product purity and yield obtained from the described process. Only reasonable and routine experimentation will be required to optimize such process conditions.

EXAMPLE 1

[0090] Silver nanowires were applied to a surface of a polymeric block copolyestercarbonate derived from resorcinol or alkylresorcinol isophthalate-terepthalate according to methods described herein. The specific copolyestercarbonate was Lexan® SLX253 IT polymer. FIG. 2 is a nanometer-scale image of the surface of the material. The nanowires are visible as bright lines on the darker surface.

[0091] FIGS. 3A and 3B show graphs of sheet resistance vs. time for this material (labeled as "Lexan® SLX PC") as compared to a known Lexan® polycarbonate (Lexan® 105 polycarbonate). As shown in the figures, the Lexan® SLX253 IT polymer had a sheet resistance 15 ± 2 Ω/sq across all measured time periods, in contrast to the prior art Lexan® polycarbonate, which had a substantially higher sheet resistance. Further, the Lexan® SLX253 IT polymer had a light transmission of 82% in the visible range of the spectrum (i.e., between 400 nm and 700 nm).

[0092] Method examples described herein can be machine or computer-implemented at least in part. Some examples can include a computer-readable medium or machine-readable medium encoded with instructions operable to configure an electronic device to perform methods as described in the above examples. An implementation of such methods can include code, such as microcode, assembly language code, a higher-level language code, or the like. Such code can include computer readable instructions for performing various methods. The code may form portions of computer program products. Further, in an example, the code can be tangibly stored on one or more volatile, non-transitory, or non-volatile tangible computer-readable media, such as during execution or at other times. Examples of these tangible computer-readable media can include, but are not limited to, hard disks, removable magnetic disks, removable optical disks (e.g., compact disks and digital video disks), magnetic cassettes, memory cards or sticks, random access memories (RAMs), read only memories (ROMs), and the like.

[0093] The above description is intended to be illustrative, and not restrictive. For example, the above-described examples (or one or more aspects thereof) may be used in combination with each other. Other aspects can be used, such as by one of ordinary skill in the art upon reviewing the above description. The Abstract is provided to comply with 37 C.F.R. §1.72(b), to allow the reader to quickly ascertain the nature of the technical disclosure. It is submitted with the understanding that it will not be used to interpret or limit the scope or meaning of the claims. Also, in the above Detailed Description, various features may be grouped together to streamline the disclosure. This should not be interpreted as intending that an unclaimed disclosed feature is essential to any claim. Rather, inventive subject matter may lie in less than all features of a particular disclosed aspect. Thus, the following claims are hereby incorporated into the Detailed Description as examples or aspects, with each claim standing on its own as a separate aspect, and it is contemplated that such aspects can be combined with each other in various combinations or permutations. The scope of the disclosure should be determined with reference to the appended claims, along with the full scope of equivalents to which such claims are entitled.

CLAIMS

We Claim:

1. An electrically-conductive material comprising a polymeric substrate and a conductive nanostructured or microstructured material adhered to at least one surface of the polymeric substrate, wherein

the polymeric substrate comprises a polymeric block copolyestercarbonate derived from resorcinol or alkylresorcinol isophthalate-terepthalate,

the polymeric block copolyestercarbonate has a glass transition temperature of at least 130 degrees Celsius (°C), and

the polymeric block copolyestercarbonate has a sheet resistance of less than 20 ohms (Ω) per square (sq).

2. The electrically-conductive material according to claim 1, wherein the polymeric block copolyestercarbonate is inherently ultraviolet resistant.

3. The electrically-conductive material according to claim 1 or 2, wherein the electrically-conductive material is transparent.

4. The electrically-conductive material according to any of claims 1 to 3, wherein the electrically-conductive material has a light transmission of greater than 80% at a wavelength of 400 to 700 nanometers (nm).

5. The electrically-conductive material according to any of claims 1 to 4, wherein the polymeric block copolyestercarbonate has good chemical resistance properties.

6. The electrically-conductive material according to any of claims 1 to 5, wherein the conductive nanostructured or microstructured material comprises silver, gold, copper, nickel, gold-plated silver and combinations thereof.

7. The electrically-conductive material according to claim 6, wherein the conductive nanostructured or microstructured material comprises silver.

8. The electrically-conductive material according to any of claims 1 to 7, wherein the polymeric block copolyestercarbonate has a glass transition temperature of about 137 °C.

9. The electrically-conductive material according to any of claims 1 to 8, wherein the conductive nanostructured or microstructured material is spray coated onto the polymeric substrate.

10. The electrically-conductive material according to any of claims 1 to 9, wherein the at least one surface is a substantially smooth surface.

11. A method for making an electrically-conductive material comprising:

applying a conductive nanostructured or microstructured material onto at least one surface of a polymeric substrate, the polymeric substrate having a glass transition temperature of at least 130 °C;

heating the at least one surface of the polymeric substrate to a temperature that is greater than the glass transition temperature of the polymeric substrate; and

applying pressure to the conductive nanostructured or microstructured material and the at least one surface to adhere the conductive nanostructured or microstructured material to the at least one surface,

wherein the polymeric substrate comprises a polymeric block copolyestercarbonate derived from resorcinol or alkylresorcinol isophthalate-terepthalate and has a sheet resistance of less than 20 ohms (Ω) per square (sq).

12. The method according to claim 11, wherein the step of applying the conductive nanostructured or microstructured material comprises spray coating, ultrasonic spray coating, roll-to-roll coating, ink jet printing, screen printing, drop casting, spin coating, dip coating, Mayer rod coating, gravure coating, slot die coating, or doctor blade coating the conductive nanostructured or microstructured material onto the at least one surface.

13. The method according to claim 12, wherein the step of applying the conductive nanostructured or microstructured material comprises spray coating the conductive nanostructured or microstructured material onto the at least one surface.

14. The method according to any of claims 11 to 13, wherein the polymeric block copolyestercarbonate is inherently ultraviolet resistant.

15. The method according to any of claims 11 to 14, wherein the electrically-conductive material is transparent.

16. The method according to any of claims 11 to 15, wherein the electrically-conductive material has a light transmission of greater than 80% at a wavelength of 400 to 700 nanometers (nm).

17. The method according to any of claims 11 to 16, wherein the polymeric block copolyestercarbonate has good chemical resistance properties.

18. The method according to any of claims 11 to 17, wherein the conductive nanostructured or microstructured material comprises silver, gold, copper, nickel, gold-plated silver and combinations thereof.

19. The method according to claim 18, wherein the conductive nanostructured or microstructured material comprises silver.

20. The method according to any of claims 11 to 19, wherein the step of applying pressure to the conductive nanostructured or microstructured material and the at least one surface causes the at least one surface to be substantially smooth.

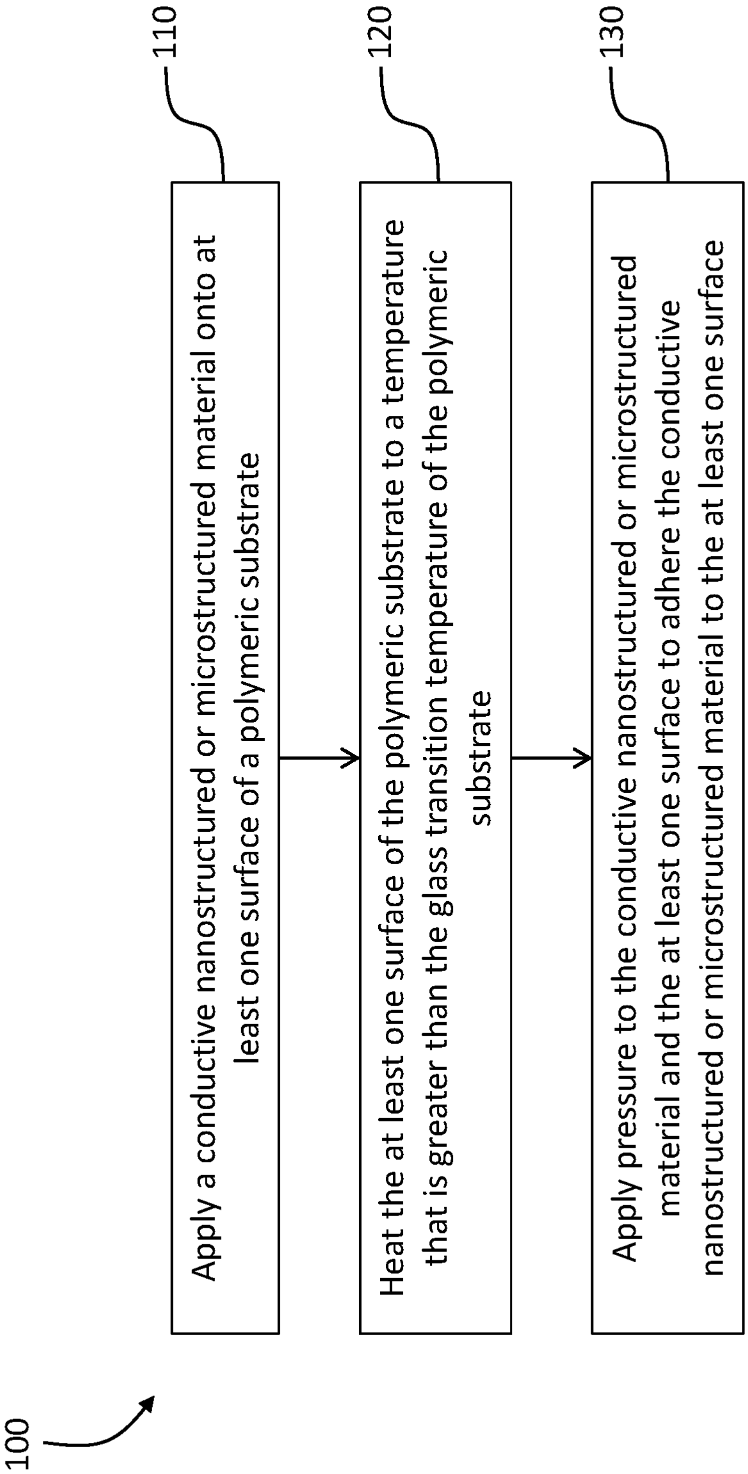

110
Apply a conductive nanostructured or microstructured material onto at least one surface of a polymeric substrate
120
Heat the at least one surface of the polymeric substrate to a temperature that is greater than the glass transition temperature of the polymeric substrate
130
Apply pressure to the conductive nanostructured or microstructured material and the at least one surface to adhere the conductive nanostructured or microstructured material to the at least one surface
100

FIG. 1

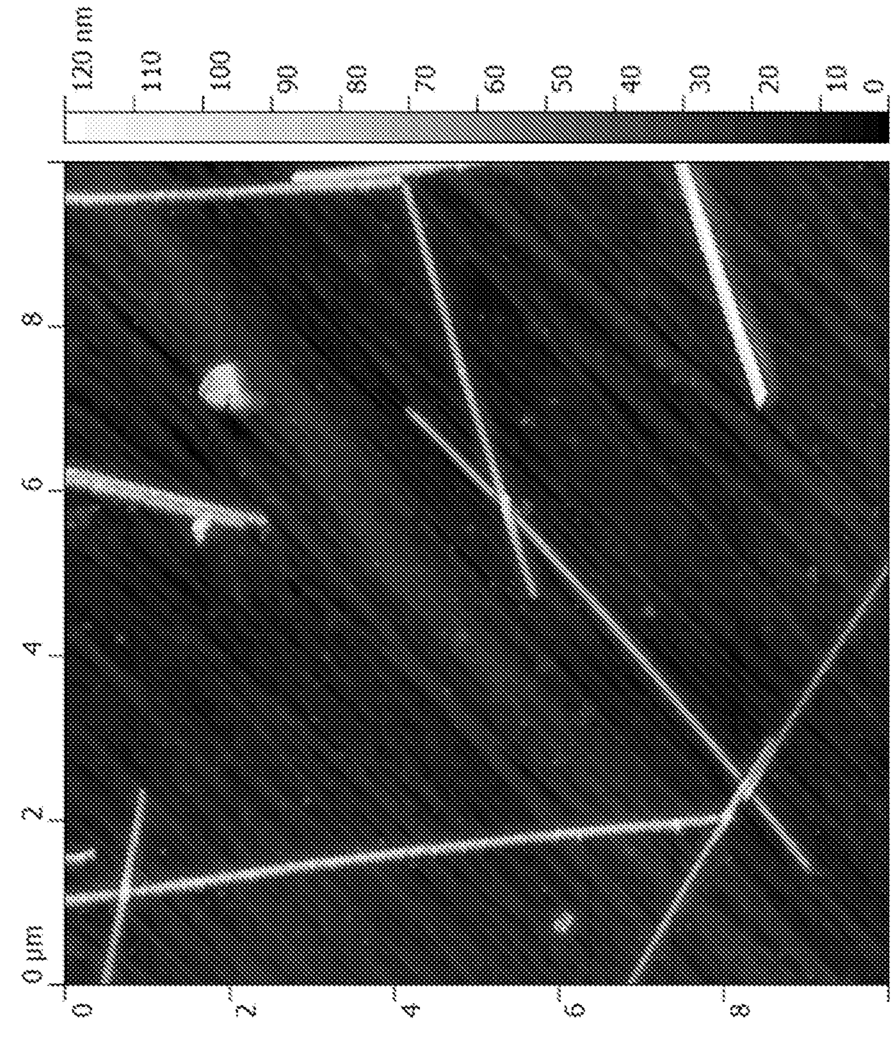
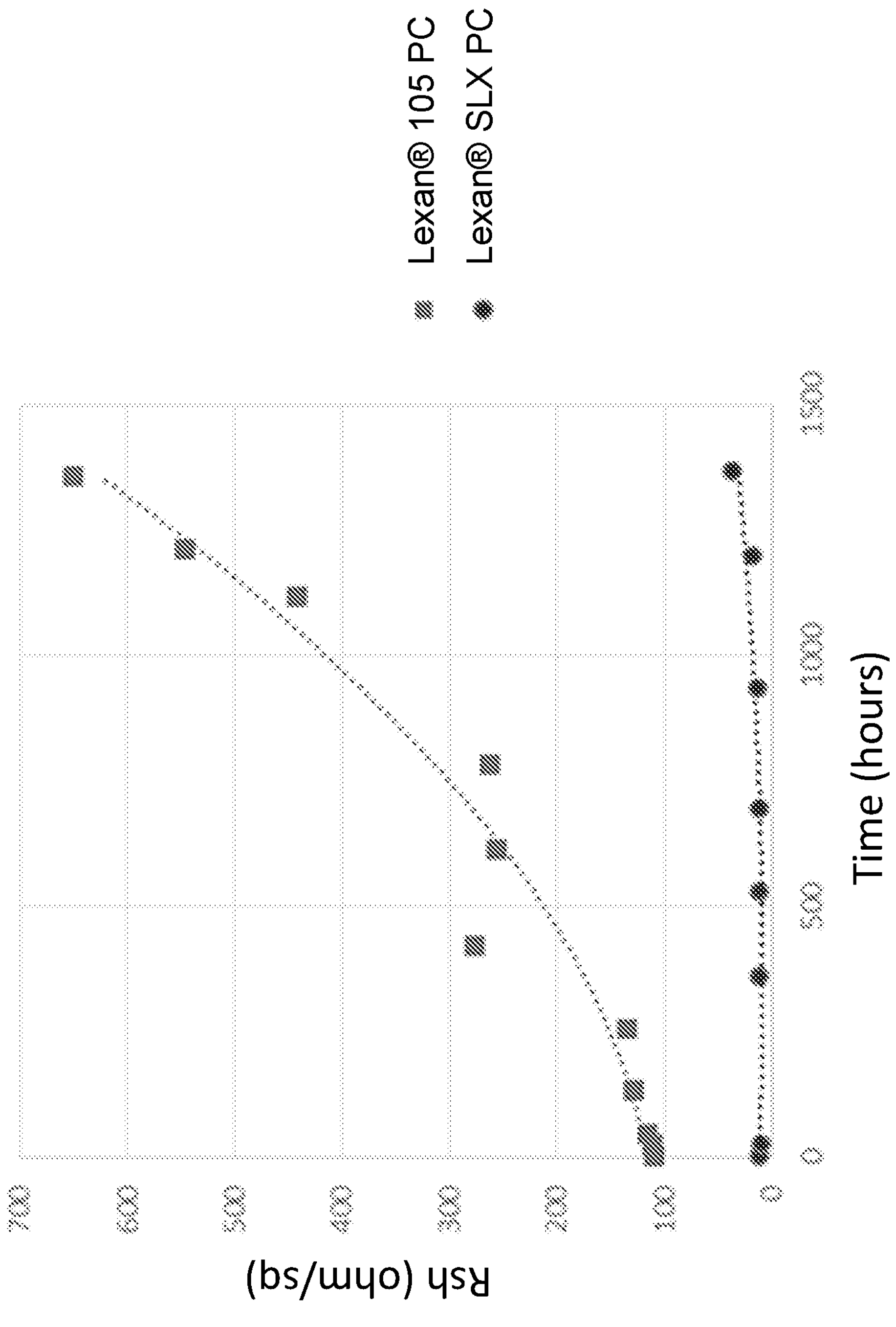


FIG. 2


Lexan® 105 PC
Lexan® SLX PC
Rsh (ohm/sq)
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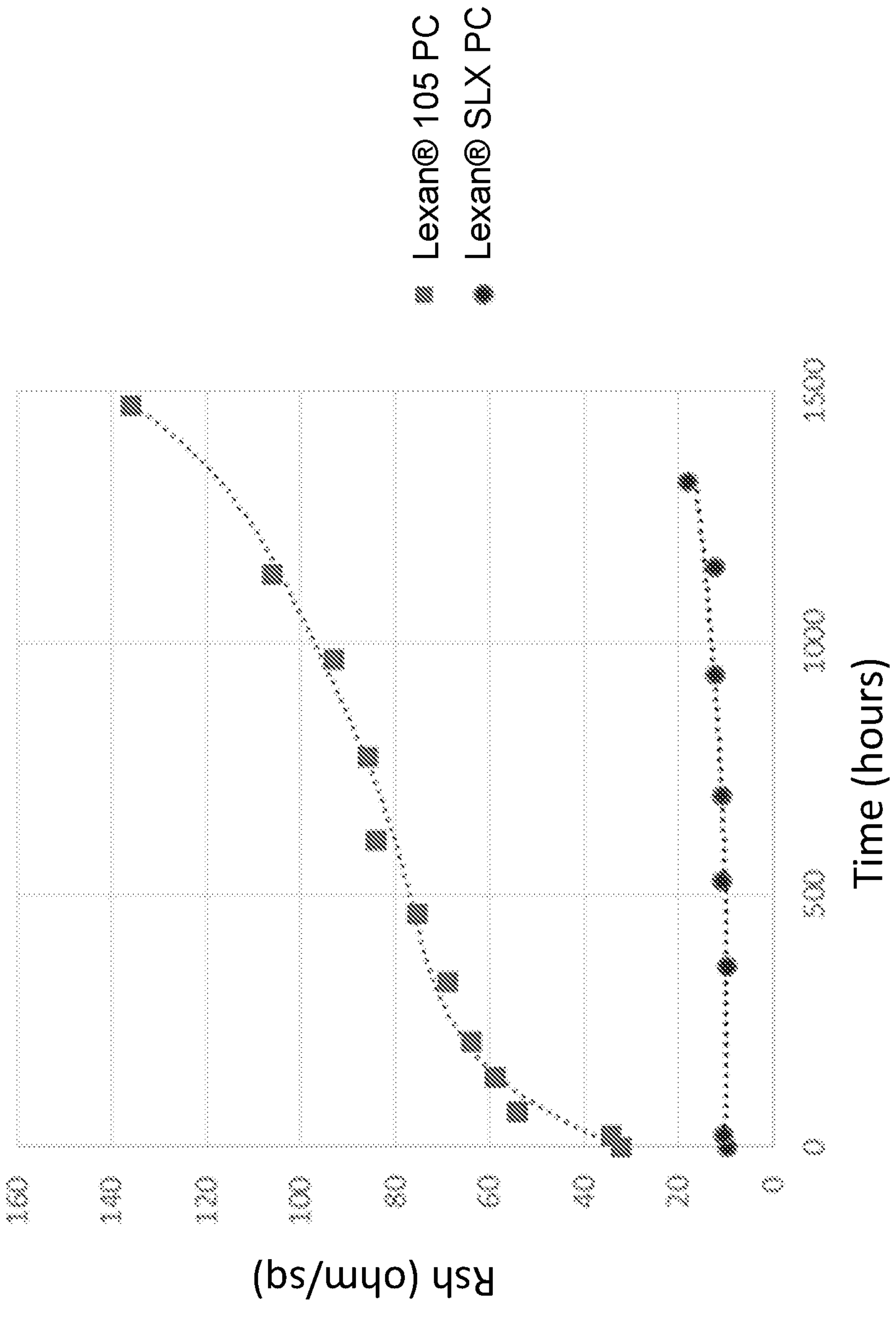
600
500
400
300
200
100
0
0
500
1000
1500
Time (hours)

FIG. 3A


Lexan® 105 PC
Lexan® SLX PC
Rsh (ohm/sq)
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20
40
60
80
100
120
140
160
0
500
1000
1500
Time (hours)

FIG. 3B

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2017/058294

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01L31/20 H01L31/0392 H01L31/048
ADD.

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)
H01L

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

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

EPO-Internal , WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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[X] Further documents are listed in the continuation of Box C.

[X] 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

"E" earlier application or patent but published on or after the international filing date

"L" documentwhich may throw doubts on priority claim(s) orwhich 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
9 March 2018	20/03/2018

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European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Chao, Oscar

1

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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1

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Information on patent family members

International application No
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