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(54) Title: PROCESS FOR MAKING AN ARTICLE FROM POLYOLEFIN AND COMPOSITION THEREOF

(57) Abstract: A method for preparing an article comprising providing a crosslinked olefin fabricated article; treating the fabricated article with a treating agent, the treating agent comprising a liquid comprising a phosphorous containing compound, and stabilizing the fabricated article by air oxidation. A method for preparing an article comprising providing an olefin resin; melt blending the olefin resin with a treating agent to provide a treated olefin resin, the treating agent comprising a phosphorous containing compound; forming a fabricated article from the treated olefin resin; crosslinking the fabricated article, and stabilizing the fabricated article by air oxidation. The composition of a precursor polyolefin article. The composition of a stabilized polyolefin article.



PROCESS FOR MAKING AN ARTICLE FROM POLYOLEFIN AND COMPOSITION THEREOF

BACKGROUND

[0001] Previously, carbonaceous articles, such as carbon fibers, have been produced primarily from polyacrylonitrile (PAN), pitch, or cellulose precursors. The process for making carbonaceous articles begins by forming a fabricated article, such as a fiber or a film, from the precursor. Precursors may be formed into fabricated articles using standard techniques for forming or molding polymers. The fabricated article is subsequently stabilized to allow the fabricated article to substantially retain shape during the subsequent heat-processing steps; without being limited by theory, such stabilization typically involves a combination of oxidation and heat and generally results in dehydrogenation, ring formation, oxidation and crosslinking of the precursor which defines the fabricated article. The stabilized fabricated article is then converted into a carbonaceous article by heating the stabilized fabricated article in an inert atmosphere. While the general steps for producing a carbonaceous article are the same for the variety of precursors, the details of those steps vary widely depending on the chemical makeup of the selected precursor.

[0002] Polyolefins have been investigated as an alternative precursor for carbonaceous articles, but a suitable and economically viable preparation process has proven elusive. Of particular interest is identifying an economical process for preparing stabilized articles from polyolefin precursors, such as stabilized articles which are suitable for subsequent processing to form carbonaceous articles. For example, maximizing mass retention during the stabilization and carbonization steps are of interest.

STATEMENT OF INVENTION

[0003] A method for preparing an article comprising providing a crosslinked olefin fabricated article; treating the fabricated article with a treating agent, the treating agent comprising a liquid comprising a phosphorous containing compound, and stabilizing the fabricated article by air oxidation.

[0004] A method for preparing an article comprising providing an olefin resin; melt blending the olefin resin with a treating agent to provide a treated olefin resin, the treating agent comprising a phosphorous containing compound; forming a fabricated article from the treated olefin resin; crosslinking the fabricated article, and stabilizing the fabricated article by air oxidation.

[0005] A precursor polyolefin article comprising an empirical formula, $\text{CH}_X\text{P}_Y\text{O}_Z$, where $1.8 \leq X \leq 2.4$; $0.001 \leq Y \leq 0.02$; and $0.01 \leq Z \leq 0.05$.

[0006] A stabilized polyolefin article comprising an empirical formula, $\text{CH}_X\text{P}_Y\text{O}_Z$, where: $0.5 \leq X \leq 1.5$; $0.002 \leq Y \leq 0.05$; and $0.1 \leq Z \leq 0.5$.

DETAILED DESCRIPTION

[0007] Unless otherwise indicated, numeric ranges, for instance “from 2 to 10,” are inclusive of the numbers defining the range (e.g., 2 and 10).

[0008] Unless otherwise indicated, ratios, percentages, parts, and the like are by weight.

[0009] Unless otherwise indicated, the crosslinkable functional group content for a polyolefin resin is characterized by the mol% crosslinkable functional groups, which is calculated as the number of mols of crosslinkable functional groups divided by the total number of mols of monomer units contained in the polyolefin.

[0010] Unless otherwise indicated, “monomer” refers to a molecule which can undergo polymerization, thereby contributing constitutional units to the essential structure of a macromolecule, for example, a polyolefin.

[0011] Unless otherwise indicated, “alkene” refers to C1 to C10 alkenes.

[0012] Unless otherwise indicated, “alkyne” refers to C1 to C10 alkynes.

[0013] In one aspect, the present disclosure describes a process for producing a stabilized fabricated article from a polyolefin resin. In one aspect, the present disclosure describes a process for producing a carbonaceous fabricated article from a polyolefin resin. Unless stated otherwise, any method or process steps described herein may be performed in any order. Polyolefins are a class of polymers produced from one or more olefin monomer. The polymers described herein may be formed from one or more types of monomers.

Polyethylene is the preferred polyolefin resin, but other polyolefin resins may be substituted. For example, a polyolefin produced from ethylene, propylene, or other alpha-olefin (for instance, 1-butene, 1-hexene, 1-octene), or a combination thereof, is also suitable. The polyolefins described herein are typically provided in resin form, subdivided into pellets or granules of a convenient size for further melt or solution processing.

[0014] In one instance, the polyolefin resin is treated with a treating agent to provide a treated olefin resin. In one instance, the treating agent is a phosphorus containing compound. An exemplary example of a suitable treating agent is phosphoric acid. Other examples of treating agents include phosphorus pentoxide and red phosphorous. The melt phase of the polyolefin resin is defined as a condition where the polyolefin resin is suitable

for forming into a fabricated article. In one instance, the melt phase is achieved by heating the resin to a temperature range where the solid resin transitions to a liquid, which temperature range will vary depending on the composition of the selected polyolefin resin, as is known in the art. In one instance, the treating agent is added to the melt phase resin. In another instance, the treating agent is introduced to the resin during the fabrication process. In another instance, the treating agent and the resin are dry blended prior to forming a melt phase; for example, the treating agent can be introduced as a masterbatch or neat. The polyolefin is treated with the treating agent such that phosphorous is contained in the fabricated article following fabrication. Any suitable treating agent which deposits phosphorous in the fabricated article may be used.

[0015] The treated olefin resin is processed to form a fabricated article. A fabricated article is an article which has been fabricated from the polyolefin resin. The fabricated article is formed using known polyolefin fabrication techniques, for example, melt or solution spinning to form fibers, film extrusion or film casting or a blown film process to form films, die extrusion or injection molding or compression molding to form more complex shapes, or solution casting. The fabrication technique is selected according to the desired geometry of the target carbonaceous article, and the desired physical properties of the same. For example, where the desired carbonaceous article is a carbon fiber, fiber spinning is a suitable fabrication technique. As another example, where the desired carbonaceous article is a carbon film, compression molding is a suitable fabrication technique.

[0016] The fabricated articles described herein are subjected to a crosslinking step. In one instance, the fabricated article has been melt blended with a treating agent prior to the crosslinking step. In one instance, the fabricated article has been melt blended without the use of a treating agent prior to the crosslinking step. A variety of methods for crosslinking polyolefins are known. In one instance, the fabricated articles are crosslinked by irradiation, such as by electron beam processing. Other crosslinking methods are suitable, for example, ultraviolet irradiation and gamma irradiation. In some instances, an initiator, such as benzophenone, may be used in conjunction with the irradiation to initiate crosslinking. In one instance, the polyolefin resins have been modified to include crosslinkable functional groups which are suitable for reacting to crosslink the polyolefin resin. Where the polyolefin resin includes crosslinkable functional groups, crosslinking may be initiated by known methods, including use of a chemical crosslinking agent, by heat, by steam, or other suitable method. In one instance, copolymers are suitable to provide a

polyolefin resin having crosslinkable functional groups where one or more alpha-olefins have been copolymerized with another monomer containing a group suitable for serving as a crosslinkable functional group, for example, dienes, carbon monoxide, glycidyl methacrylate, acrylic acid, vinyl acetate, maleic anhydride, or vinyl trimethoxy silane (VTMS) are among the monomers suitable for being copolymerized with the alpha-olefin. Further, the polyolefin resin having crosslinkable functional groups may also be produced from a poly(alpha-olefin) which has been modified by grafting a functional group moiety onto the base polyolefin, wherein the functional group is selected based on its ability to subsequently enable crosslinking of the given polyolefin. For example, grafting of this type may be carried out by use of free radical initiators (such as peroxides) and vinyl monomers (such as VTMS, dienes, vinyl acetate, acrylic acid, methacrylic acid, acrylic and methacrylic esters such as glycidyl methacrylate and methacryloxypropyl trimethoxysilane, allyl amine, p-aminostyrene, dimethylaminoethyl methacrylate) or via azido-functionalized molecules (such as 4-[2-(trimethoxysilyl)ethyl]benzenesulfonyl azide). Polyolefin resins having crosslinkable functional groups may be produced from a polyolefin resin, or may be purchased commercially. Examples of commercially available polyolefin resins having crosslinkable functional groups include SI-LINK sold by The Dow Chemical Company, PRIMACOR sold by The Dow Chemical Company, EVAL resins sold by Kuraray, and LOTADER AX8840 sold by Arkema.

[0017] As noted above, at least a portion of the polyolefin is crosslinked to yield a crosslinked fabricated article. In some embodiments, crosslinking is carried out via chemical crosslinking. Thus, in some embodiments, the crosslinked fabricated article is a fabricated article which has been treated with one or more chemical agents to crosslink the crosslinkable functional groups of the polyolefin resin having crosslinkable functional groups. Such chemical agent functions to initiate the formation of intramolecular chemical bonds between the crosslinkable functional groups or reacts with the crosslinkable functional groups to form intramolecular chemical bonds, as is known in the art. Chemical crosslinking causes the crosslinkable functional groups to react to form new bonds, forming linkages between the various polymer chains which define the polyolefin resin having crosslinkable functional groups. The chemical agent which effectuates the crosslinking is selected based on the type of crosslinkable functional group(s) included in the polyolefin resin; a diverse array of reactions are known which crosslink crosslinkable functional groups via intermolecular and intramolecular chemical bonds. A suitable chemical agent is

selected which is known to crosslink the crosslinkable functional groups present in the fabricated article to produce the crosslinked fabricated article. For example, without limiting the present disclosure, if the crosslinkable functional group attached to the polyolefin is a vinyl group, suitable chemical agents include free radical initiators such as peroxides or azo-bis nitriles, for example, dicumyl peroxide, dibenzoyl peroxide, t-butyl peroctoate, azobisisobutyronitrile, and the like. If the crosslinkable functional group attached to the polyolefin is an acid, such as a carboxylic acid, or an anhydride, or an ester, or a glycidoxy group, a suitable chemical agent can be a compound containing at least two nucleophilic groups, including dinucleophiles such as diamines, diols, dithiols, for example ethylenediamine, hexamethylenediamine, butane diol, or hexanedithiol. Compounds containing more than two nucleophilic groups, for example glycerol, sorbitol, or hexamethylene tetramine can also be used. Mixed di- or higher- nucleophiles, which contain at least two different nucleophilic groups, for example ethanolamine can also be suitable chemical agents. If the crosslinkable functional group attached to the polyolefin is a mono-, di- or tri- alkoxy silyl group, water, and Lewis or Bronsted acid or base catalysts can be used as suitable chemical agents. For example, without limiting the present disclosure, Lewis or Bronsted acid or base catalysts include aryl sulfonic acids, sulfuric acid, hydroxides, zirconium alkoxides or tin reagents.

[0018] Crosslinking the fabricated article is preferred to ensure that the fabricated article retains its shape at the elevated temperatures required for the subsequent processing steps. Without crosslinking, polyolefin resins typically soften, melt or otherwise deform or breakdown at elevated temperatures. Crosslinking adds thermal stability to the fabricated article.

[0019] In one instance, the crosslinked fabricated article is treated with the treating agent. As described herein, the treating agent is phosphorous-containing compound. An exemplary example of a suitable treating agent is phosphoric acid. Other examples of treating agents include elemental phosphorous, phosphorus pentoxide, organophosphate, or organophosphite. Other examples of treating agents include phosphate esters; phosphonic acids and their esters; phosphonic acid anhydride; phosphonic acid salts; phosphinic acids and their esters; phosphinic acid anhydride; phosphinic acid salts; phosphite and phosphite derivatives; phosphonate and phosphonate derivatives; phosphinate and phosphinate derivatives; phosphonite and phosphonite derivatives; phosphinite and phosphinite derivatives; phosphine and phosphine derivatives; phosphine ligands; phosphine oxides;

chalcogenides; phosphalkenes; phosphalkynes; phosphonium salts; phosphoranes; phosphorus halides; and phosphorylating compounds. The crosslinked fabricated article is treated with the treating agent by any mechanism known in the art, such as spraying, dipping, or imbibing. The treating agent may be introduced in a suitable liquid form, for example neat, or as part of a solution, or as a suspension in a liquid. The treating agent may be introduced as part of a continuous process or as part of a batch process. In one instance, the treating agent is introduced during the melt blend step. In one instance, the treating agent is introduced after the crosslinking step. In one instance, the treating agent is introduced during both the melt blend step and after the crosslinking step.

[0020] The crosslinked fabricated article is heated in an oxidizing environment to yield a stabilized fabricated article. In some embodiments, the temperature for stabilizing the crosslinked fabricated article is at least 120 °C, preferably at least 190 °C. In some embodiments, the temperature for stabilizing the crosslinked fabricated article is no more than 400 °C, preferably no more than 300 °C. In one instance, the crosslinked fabricated article is introduced to a heating chamber which is already at the desired temperature. In another instance, the fabricated article is introduced to a heating chamber at or near ambient temperature, which chamber is subsequently heated to the desired temperature. In some embodiments the heating rate is at least 1 °C/minute. In other embodiments the heating rate is no more than 15 °C/minute. In yet another instance, the chamber is heated step wise, for instance, the chamber is heated to a first temperature for a time, such as, 120 °C for one hour, then is raised to a second temperature for a time, such as 180 °C for one hour, and third is raised to a holding temperature, such as 250 °C for 10 hours. The stabilization process involves holding the crosslinked fabricated article at the given temperature for periods up to 100 hours depending on the dimensions of the fabricated article. The stabilization process yields a treated stabilized fabricated article which is a precursor for a carbonaceous article. Without being limited by theory, the stabilization process oxidizes the crosslinked fabricated article and causes changes to the hydrocarbon structure that increases the crosslink density while decreasing the hydrogen/carbon ratio of the crosslinked fabricated article. Without being limited by theory, the stabilization process introduces phosphorous to the hydrocarbon structure.

[0021] Unexpectedly, it has been found that including a treating agent in the fabricated article during the stabilization step improves mass retention of the subsequently produced carbonaceous article. It has also been found that incorporating phosphorous in the

crosslinked fabricated article improves form-retention of the subsequently produced carbonaceous article.

[0022] In another aspect, the present disclosure describes a treated stabilized fabricated article which is formed from a polyolefin precursor (resin). In one instance, the treated stabilized fabricated article is formed according to the process described herein.

[0023] In yet another aspect, a carbonaceous article and a process for making the same are provided. Carbonaceous articles are articles which are rich in carbon; carbon fibers, carbon sheets and carbon films are examples of carbonaceous articles. Carbonaceous articles have many applications, for example, carbon fibers are commonly used to reinforce composite materials, such as in carbon fiber reinforced epoxy composites, while carbon discs or pads are used for high performance braking systems.

[0024] The carbonaceous articles described herein are prepared by carbonizing the stabilized fabricated article by heat-treating the treated stabilized fabricated articles in an inert environment. The inert environment is an environment surrounding the treated stabilized fabricated article that shows little reactivity with carbon at elevated temperatures, preferably a high vacuum or an oxygen-depleted atmosphere, more preferably a nitrogen atmosphere or an argon atmosphere. It is understood that trace amounts of oxygen may be present in the inert atmosphere. In one instance, the temperature of the inert environment is at or above 600 °C. Preferably, the temperature of the inert environment is at or above 800°C. In one instance, the temperature of the inert environment is no more than 3000 °C. In one instance, the temperature is from 1400-2400 °C. Temperatures at or near the upper end of that range will produce a graphite article, while temperatures at or near the lower end of the range will produce a carbon article.

[0025] In order to prevent bubbling or damage to the fabricated article during carbonization, it is preferred to heat the inert environment in a gradual or stepwise fashion. In one embodiment, the treated stabilized fabricated article is introduced to a heating chamber containing an inert environment at or near ambient temperature, which chamber is subsequently heated over a period of time to achieve the desired final temperature. The heating schedule can also include one or more hold steps for a prescribed period at the final temperature or an intermediate temperature or a programmed cooling rate before the article is removed from the chamber.

[0026] In yet another embodiment, the chamber containing the inert environment is subdivided into multiple zones, each maintained at a desired temperature by an appropriate

control device, and the treated stabilized fabricated article is heated in a stepwise fashion by passage from one zone to the next via an appropriate transport mechanism, such as a motorized belt. In the instance where a treated stabilized fabricated article is a fiber, this transport mechanism can be the application of a traction force to the fiber at the exit of the carbonization process while the tension in the stabilized fiber is controlled at the inlet.

[0027] In one instance, the present disclosure describes a precursor polyolefin article comprising an empirical formula, $\text{CH}_X\text{P}_Y\text{O}_Z$, where $1.8 \leq X \leq 2.2$; $0.004 \leq Y \leq 0.02$; and $0.14 \leq Z \leq 0.5$. In one instance, $1.8 \leq X \leq 2.4$. In one instance, $0.001 \leq Y \leq 0.02$. In one instance, $0.01 \leq Z \leq 0.05$. In one instance, $X = 2.1$. In one instance, $Y = 0.008$. In one instance, $Z = 0.028$.

[0028] In one instance, the present disclosure describes a stabilized polyolefin article comprising an empirical formula, $\text{CH}_X\text{P}_Y\text{O}_Z$ where $0.5 \leq X \leq 1.5$; $0.002 \leq Y \leq 0.05$; and $0.1 \leq Z \leq 0.5$. In one instance, $0.617 \leq X \leq 1.245$. In one instance, $0.004 \leq Y \leq 0.028$. In one instance, $0.209 \leq Z \leq 0.355$.

[0029] Some embodiments of the invention will now be described in detail in the following Examples.

[0030] In the Examples, overall mass yield is calculated as the product of oxidation mass yield and carbonization mass yield (calculated as provided below). PHR refers to parts per hundred resin (mass basis). MI refers to melt index which is a measure of melt flow rate. Wt% refers to parts per 100 total parts, mass basis. PE refers to polyethylene. Definitions of measured yields:

[0031] Oxidation mass yield: $Y_O = \frac{m_{OX}}{m_{PE}}$

[0032] Carbonization mass yield: $Y_C = \frac{m_{CF}}{m_{OX}}$

[0033] Overall mass yield: $Y_M = Y_O Y_C$

[0034] Overall mass yield (carbonaceous mass per initial mass of PE): $Y_{M,PE} = \frac{Y_O Y_C}{M_{\%PE}}$

[0035] Where m_{PE} is the initial mass of polyethylene; m_{OX} is the mass remaining after oxidation; m_{CF} is the mass remaining after carbonization; $M_{\%PE}$ is the mass % of polyethylene in the origin formed article.

[0036] Soxhlet extraction is a method for determining the gel fraction and swell ratio of crosslinked ethylene plastics, also referred to herein as hot xylenes extraction. As used herein, Soxhlet extraction is conducted according to ASTM Standard D2765-11 "Standard Test Methods for Determination of Gel Content and Swell Ratio of Crosslinked Ethylene

Plastics.” In the method employed, a crosslinked fabricated article between 0.050 - 0.500 g is weighed and placed into a cellulose-based thimble which is then placed into a Soxhlet extraction apparatus with sufficient quantity of xylenes. Soxhlet extraction is then performed with refluxing xylenes for at least 12 hours. Following extraction, the thimbles are removed and the crosslinked fabricated article is dried in a vacuum oven at 80 °C for at least 12 hours and then weighed, thereby providing a Soxhlet-treated article. The gel fraction (%) is then calculated from the weight ratio (Soxhlet-treated article)/(crosslinked fabricated article). The TGA Method for determining percent stabilization by sulfonation is as follows: a TA Instruments Thermal Gravimetric Analyzer (TGA) Q5000 or Discovery Series TGA is used. Using ~ 10-20 mg for the analysis, the sample is heated at 10 °C/min to 800 °C under nitrogen. The final weight of the sample at 800 °C is referred to as the char yield. The VTMS content of the VTMS grafted resins was determined by ¹³C NMR.

[0037] The treated articles are submitted for elemental analysis to determine the carbon, hydrogen, phosphorous, sulfur, and oxygen content. A Thermo Model Flash EA1112 Combustion CHNS/O Analyzer is used for determining carbon, hydrogen, phosphorous, sulfur, and oxygen components. Phosphorus is detected by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Perkin Elmer Optima 7300DV ICP atomic emission spectrometer.

Comparative Examples 1-2

[0038] An ethylene/octene copolymer (density = 0.941 g/cm³; MI = 34 g/10 min, 190°C/2.16 kg) is reactive extruded with vinyl trimethoxysilane (VTMS) to form a VTMS-grafted ethylene/octene copolymer (MI = 19 g/10 min, 190 °C/2.16 kg; 1.4 wt% grafted silane content determined by ¹³C NMR) precursor resin. The VTMS-grafted precursor resin is melt spun to form fibers with the following properties: 1573 filaments, 1945.8 total denier, 2.25 gf/den, 12.17% elongation-to-break. Two tows of the prepared fibers, identified as C1 and C2, are continuously treated in a vessel containing an isopropanol solution with 5 wt% of an aryl sulfonic acid, Nacure B201 for 5 seconds. The treated fibers are allowed to dry cure for 3 days. The fibers are subsequently moisture cured at 80 °C (80% relative humidity) for 5 days. The mean gel fraction is determined to be 60.0% by Soxhlet extraction. The crosslinked fibers are oxidized at 270 °C for 5 hours under air (21% oxygen content). The fibers are weighed before and after oxidation. The composition of the oxidized fibers of C1 is 70.8 wt% carbon, 7.4 wt% hydrogen, and 20.1 wt% oxygen; the composition of the oxidized fibers of C2 is 74.8 wt% carbon, 9.3 wt% hydrogen, and

15.9 wt% oxygen. Oxidized crosslinked fibers are then carbonized in a TGA instrument under nitrogen from 25°C to 800°C using a ramp of 10°C/min. Carbonization mass yield is determined as char yield at 800°C. Oxidation, carbonization, and overall mass yields are reported in Table 1. It is noted, that since the articles did not undergo treatment with a phosphorous-containing compound, no Phosphorous was measured in the oxidized articles, as shown Tables 1 and 12-16.

Table 1

Example	Oxidation Mass Yield (%)	Carbonization Mass Yield (%)	Overall Mass Yield (%)
C1	44.2	53.4	23.6
C2	43.7	54.6	23.9

Examples 3-8

[0039] 6 tows of Crosslinked fibers, identified as 3, 4, 5, 6, 7 and 8, prepared as in Comparative Examples 1-2 are dipped in aqueous solutions of phosphoric acid for 1 minute each. The weight uptake of solution and the amount of phosphoric acid contained in that liquid uptake is recorded in Table 2.

Table 2

Example	Phosphoric Acid Concentration (%)	Absorbed Liquid (g/g PE)	Phosphoric Acid Absorbed (g/g PE)
3	10	0.293	0.035
4	10	0.209	0.021
5	20	0.585	0.050
6	20	0.578	0.056
7	30	0.589	0.053
8	30	0.613	0.054

[0040] The phosphoric acid-treated crosslinked fibers are oxidized at 270°C for 5 hours under air (21% oxygen content). The fibers are weighed before and after oxidation. The composition of the oxidized fibers in Examples 3 and 4 is 67.0 wt% carbon, 5.2 wt% hydrogen, 22.8 wt% oxygen, and 1.7 wt% phosphorous. The composition of the oxidized fibers in Examples 5 and 6 is 67.9 wt% carbon, 6.0 wt% hydrogen, 18.9 wt% oxygen, and

2.7 wt% phosphorous. The composition of the oxidized fibers in Examples 7 and 8 is 68.0 wt% carbon, 7.1 wt% hydrogen, 19.7 wt% oxygen, and 3.6 wt% phosphorous. Oxidized crosslinked fibers are then carbonized in a TGA instrument under nitrogen from 25°C to 800°C using a ramp of 10°C/min. Carbonization mass yield is determined as char yield at 800°C. Oxidation, carbonization, and overall mass yields are reported in Table 3. Tables 12-16 report the elemental composition of Examples 3-8.

Table 3

Example	Oxidation Mass Yield (%)	Carbonization Mass Yield (%)	Overall Mass Yield (%)
3	78.7	39.6	31.1
4	72.9	58.8	42.9
5	88.9	51.0	45.3
6	85.7	58.3	50.0
7	92.9	53.6	49.8
8	98.9	51.0	50.4

Comparative Examples 9-10

[0041] An ethylene/octene copolymer (density = 0.941 g/cm³; MI = 34 g/10 min, 190 °C/2.16 kg) is reactive extruded with vinyl trimethoxysilane (VTMS) to form a VTMS-grafted ethylene/octene copolymer (MI = 19 g/10 min, 190 °C/2.16 kg; 1.2 wt% grafted silane content determined by ¹³C NMR) precursor resin. The VTMS-grafted precursor resin is melt spun to form fibers with the following mean properties: 1573 filaments, 3.17 gf/den, and 9.2% elongation-to-break. Two tows of the fiber, identified as C9 and C10 are fed continuously to a series of stirred tank reactors to crosslink the fibers. Reactor 1 contains 6% oleum maintained at 90 °C. Reactor 2 contains 96% sulfuric acid maintained at 120 °C. Reactor 3 contains 50% sulfuric acid maintained at room temperature. Reactor 4 contains deionized water maintained at room temperature. Residence time in each reactor is 1.25 min. The mean gel fraction of the fiber is 66.6%, as determined by Soxhlet extraction. The resulting dark brown/black fiber yields 4% char when heated in a TGA instrument to 800 °C under nitrogen. The crosslinked fibers are oxidized at 270 °C for 5 hours under air (21% oxygen content). The fibers are weighed before and after oxidation. The composition of the oxidized fibers of C9 is 67.5 wt% carbon, 4.7 wt% hydrogen, and 21.8 wt% oxygen.

Oxidized crosslinked fibers are then carbonized in a TGA instrument under nitrogen from 25 °C to 800 °C using a ramp of 10°C/min. Carbonization mass yield is determined as char yield at 800 °C. Oxidation, carbonization, and overall mass yields are reported in Table 4. Tables 12-16 report the elemental composition of Comparative Example 9.

Table 4

Example	Oxidation Mass Yield (%)	Carbonization Mass Yield (%)	Overall Mass Yield (%)
C9	13.8	60.3	8.4
C10	7.7	61.3	4.7

Examples 11-16

[0042] Six tows of crosslinked fibers, identified as 11, 12, 13, 14, 15 and 16, prepared as in Comparative Examples 9-10 are dipped in aqueous solutions of phosphoric acid for 1 minute each. The weight uptake of solution and the amount of phosphoric acid contained in that liquid uptake is recorded in Table 5.

Table 5

Example	Phosphoric Acid Concentration (%)	Phosphoric Acid Absorbed (g/g PE)
11	10	0.025
12	10	0.018
13	20	0.099
14	20	0.098
15	30	0.150
16	30	0.156

[0043] The phosphoric acid-treated crosslinked fibers are oxidized at 270 °C for 5 hours under air (21% oxygen content). The fibers are weighed before and after oxidation. The composition of the oxidized fibers in Examples 11 and 12 is 61.9 wt% carbon, 3.2 wt% hydrogen, 29.3 wt% oxygen, and 2.3 wt% phosphorous. The composition of the oxidized fibers in Examples 13 and 14 is 61.3 wt% carbon, 3.5 wt% hydrogen, 28.0 wt% oxygen, and 3.8 wt% phosphorous. The composition of the oxidized fibers in Examples 15 and 16 is 60.8 wt% carbon, 3.8 wt% hydrogen, 27.9 wt% oxygen, and 4.3 wt% phosphorous.

Oxidized crosslinked fibers are then carbonized in a TGA instrument under nitrogen from 25 °C to 800 °C using a ramp of 10 °C/min. Carbonization mass yield is determined as char yield at 800 °C. Additionally, oxidized crosslinked samples are then carbonized in a TGA instrument under nitrogen from 25 °C to 1500 °C using a ramp of 10 °C/min. Oxidation, carbonization, and overall mass yields are reported in Table 3. Tables 12-16 report the elemental composition of Examples 11-16.

Table 6

Example	Oxidation Mass Yield (%)	Carbonization Mass Yield (%), 800°C	Overall Mass Yield (%), 800°C	Carbonization Mass Yield (%), 1500°C	Overall Mass Yield (%), 1500°C
11	69.0	60.2	41.5	42.6	29.4
12	81.3	62.6	50.9	N/A	N/A
13	93.1	60.6	57.3	45.2	42.0
14	94.5	60.4	57.1	N/A	N/A
15	100.5	61.1	61.4	44.4	44.6
16	100.3	61.0	61.2	N/A	N/A

Comparative Example 17

[0044] Powdered polyethylene sold from Equistar Chemicals, Microthene FA 7000 (20 micron particle size, density = 0.953 g/mL, melt index = 10.5 g/10min, melting point = 134°C) is weighed in a vial (300 mg) with 6 mg Esacure One (sold by Lamberti, Inc. as a photoinitiated crosslinker for polyethylene and described as a difunctional alpha hydroxyketone). This mixture is pressed into a ~2 mil film at 180 °C at 20,000 psi for 10 seconds. Eighty-four (84) films are produced using this procedure. The films are irradiated with a medium-pressure mercury light at 600 W for 30 seconds 1 inch from the light source to crosslink the films. The crosslinked films are subjected to air oxidation in a convection oven at 270 °C for 5 hours, and carbonized in a TGA under nitrogen to 800 °C. The average oxidation mass yield is 41.2 ± 4.0 %. The average carbonization mass yield is 34.6 ± 7.2 %. The average overall mass yield is 14.08 ± 2.4 %.

Example 18

[0045] Powdered polyethylene sold from Equistar Chemicals, Microthene FA 7000 (20 micron particle size, density = 0.953 g/mL, melt index = 10.5 g/10min, melting point =

134°C) is weighed in a vial (300 mg) with 6 mg Esacure One (sold by Lamberti, Inc. as a photoinitiated crosslinker for polyethylene and described as a difunctional alpha hydroxyketone). To this mixture, ~20 mg of Exolit RP 6500 (~50% solids red phosphorus encapsulated in liquid epoxy; sold by Clariant) is added. This mixture is then pressed into a ~2 mil film at 180 °C at 20,000 psi for 10 seconds. The film is then irradiated with a medium-pressure mercury light at 600 W for 30 seconds 1 inch from the light source to crosslink the film. The crosslinked phosphorus-doped film is subjected to air oxidation in a convection oven at 270 °C for 5 hours, and carbonized in a TGA under nitrogen to 800 °C. The oxidation, carbonization, and overall mass yields are 70%, 65%, and 46%, respectively.

Example 19

[0046] Powdered polyethylene sold from Equistar Chemicals, Microthene FA 7000 (20 micron particle size, density = 0.953 g/mL, melt index = 10.5 g/10min, melting point = 134°C) is weighed in a vial (300 mg) with 6 mg Esacure One (sold by Lamberti, Inc. as a photoinitiated crosslinker for polyethylene and described as a difunctional alpha hydroxyketone) and to this solid mixture, 15 mg of phosphorus pentoxide is added. This mixture is then pressed into a ~2 mil film at 180 °C at 20,000 psi for 10 seconds. The film is irradiated with a medium-pressure mercury light at 600 W for 30 seconds 1 inch from the light source to crosslink the film. The composition of the precursor crosslinked P₂O₅-doped film is 81.7 wt% carbon, 14.1 wt% hydrogen, 3.1 wt% oxygen, and 1.7 wt% phosphorus. The crosslinked P₂O₅-doped film is subjected to air oxidation in a convection oven at 270 °C for 5 hours. The composition of the oxidized P₂O₅-doped film is 70.9 wt% carbon, 6.3 wt% hydrogen, 20.2 wt% oxygen, and 0.8 wt% phosphorus. The oxidized film is carbonized in a TGA under nitrogen to 800 °C. The oxidation, carbonization, and overall mass yields are 65.5%, 55.4%, and 36.3%, respectively. Tables 7-11 report the elemental composition of Example 19 precursor film. Tables 12-16 report the elemental composition of Example 19 oxidized film.

Table 7

Precursor Example	C (wt%)	H (wt%)	N (wt%)	O (wt%)	P (wt%)
19	81.7	14.1	0.0	3.1	1.7

Table 8

Precursor Example	H/C (wt/wt)	O/C (wt/wt)	P/C (wt/wt)
19	0.173	0.0376	0.0206

Table 9

Precursor Example	C (mol%)	H (mol%)	N (mol%)	O (mol%)	P (mol%)
19	32.313	66.517	0.0	0.009	0.0003

Table 10

Precursor Example	H/C (mol/mol)	O/C (mol/mol)	P/C (mol/mol)
19	2.06	0.0282	0.008

Table 11

Precursor Example	CH _x P _y O _z
19	CH _{2.06} P _{0.008} O _{0.0282}

Table 12

Oxidized Example	C (wt%)	H (wt%)	N (wt%)	P (wt%)	O (wt%)
C1	70.8	7.4	0.0	-	20.1
C2	74.8	9.3	0.0	0.0	15.9
3-4	67.0	5.2	0.0	1.7	22.8
5-6	67.9	6.0	0.0	2.7	18.9
7-8	68.0	7.1	0.0	3.6	19.7
C9	67.5	4.7	0.0	-	21.8
11-12	61.9	3.2	0.0	2.3	29.3
13-14	61.3	3.5	0.0	3.8	28.0
15-16	60.8	3.8	0.0	4.3	27.9
19	70.9	6.3	0.0	0.8	20.2

Table 13

Oxidized Example	H/C (wt/wt)	P/C (wt/wt)	O/C (wt/wt)
C1	0.1045	-	0.2836
C2	0.1243	0.0000	0.2126
3-4	0.0777	0.0256	0.3401
5-6	0.0884	0.0401	0.2781
7-8	0.1044	0.0533	0.2901
C9	0.0696		0.3233
11-12	0.0517	0.0375	0.4734
13-14	0.0563	0.0617	0.4568
15-16	0.0625	0.0713	0.4589
19	0.0889	0.0111	0.2849

Table 14

Oxidized Example	C (mol%)	H (mol%)	N (mol%)	P (mol%)	O (mol%)
C1	40.7	50.7	0.0	0.0	8.7
C2	37.8	56.1	0.0	0.0	6.0
3-4	45.6	42.3	0.0	0.5	11.6
5-6	43.9	46.3	0.0	0.7	9.2
7-8	40.3	50.1	0.0	0.8	8.8
C9	48.2	40.1	0.0	0.0	11.7
11-12	50.3	31.1	0.0	0.7	17.9
13-14	49.1	32.9	0.0	1.2	16.8
15-16	47.2	35.2	0.0	1.3	16.3
19	43.9	46.5	0.0	0.2	9.4

Table 15

Oxidized Example	H/C (mol/mol)	P/C (mol/mol)	O/C (mol/mol)
C1	1.2467	0.0000	0.2129
C2	1.4830	0.0000	0.1596
3-4	0.9264	0.0099	0.2553
5-6	1.0540	0.0155	0.2087
7-8	1.2454	0.0207	0.2178
C9	0.8305	0.0000	0.2427
11-12	0.6171	0.0145	0.3554
13-14	0.6713	0.0239	0.3429
15-16	0.7455	0.0277	0.3445
19	1.0599	0.0043	0.2139

Table 16

Oxidized Example	$\text{CH}_x\text{P}_y\text{O}_z$
C1	$\text{CH}_{1.247}\text{O}_{0.213}$
C2	$\text{CH}_{1.483}\text{O}_{0.160}$
3-4	$\text{CH}_{0.926}\text{P}_{0.010}\text{O}_{0.255}$
5-6	$\text{CH}_{1.054}\text{P}_{0.016}\text{O}_{0.209}$
7-8	$\text{CH}_{1.245}\text{P}_{0.021}\text{O}_{0.218}$
C9	$\text{CH}_{0.831}\text{O}_{0.243}$
11-12	$\text{CH}_{0.617}\text{P}_{0.015}\text{O}_{0.355}$
13-14	$\text{CH}_{0.671}\text{P}_{0.024}\text{O}_{0.343}$
15-16	$\text{CH}_{0.746}\text{P}_{0.028}\text{O}_{0.345}$
19	$\text{CH}_{1.060}\text{P}_{0.004}\text{O}_{0.214}$

WHAT IS CLAIMED IS:

1. A method for preparing an article comprising:
 - (a) providing a crosslinked olefin fabricated article;
 - (b) treating the fabricated article with a treating agent, the treating agent comprising a liquid comprising a phosphorous containing compound, and
 - (c) stabilizing the fabricated article by air oxidation.
2. The method of claim 1, further comprising (d) carbonizing the fabricated article.
3. The method of any one of claims 1-2, wherein the treating agent is phosphoric acid, organophosphate, or organophosphite.
4. The method of claim 3, wherein the treating agent is selected from the group consisting of: phosphate esters; phosphonic acids and their esters; phosphonic acid anhydride; phosphonic acid salts; phosphinic acids and their esters; phosphinic acid anhydride; phosphinic acid salts; phosphite and phosphite derivatives; phosphonate and phosphonate derivatives; phosphinate and phosphinate derivatives; phosphonite and phosphonite derivatives; phosphinite and phosphinite derivatives; phosphine and phosphine derivatives; phosphine ligands; phosphine oxides; chalcogenides; phosphalkenes; phosphalkynes; phosphonium salts; phosphoranes; phosphorus halides; and phosphorylating compounds.
5. The method any one of claims 1-4, wherein step (c) comprises heating the crosslinked fabricated article at or above 120 °C.
6. The method of any one of claims 1-5, wherein step (c) comprises converting said polyolefin resin to a fabricated article by fiber spinning, film extrusion casting, blown film processing, profile extrusion through a die, injection molding, solution casting or compression molding.
7. A method for preparing an article comprising:
 - (a) providing an olefin resin;
 - (b) melt blending the olefin resin with a treating agent to provide a treated olefin resin, the treating agent comprising a phosphorous containing compound;
 - (c) forming a fabricated article from the treated olefin resin;
 - (d) crosslinking the fabricated article, and

- (e) stabilizing the fabricated article by air oxidation.
8. The method of claim 7, further comprising (d) carbonizing the fabricated article.
9. The method of any one of claims 7-8, wherein the treating agent is phosphorus pentoxide, or red phosphorous.
10. The method any one of claims 7-9, wherein step (c) comprises heating the crosslinked fabricated article at or above 120 °C.
11. The method of any one of claims 7-10, wherein step (c) comprises converting said polyolefin resin to a fabricated article by fiber spinning, film extrusion casting, blown film processing, profile extrusion through a die, injection molding, solution casting or compression molding.
12. A precursor polyolefin article comprising an empirical formula, $\text{CH}_X\text{P}_Y\text{O}_Z$, where:
 $1.8 \leq X \leq 2.4$;
 $0.001 \leq Y \leq 0.02$; and
 $0.01 \leq Z \leq 0.05$.
13. The precursor polyolefin article of claim 12, where:
 $2.0 \leq X \leq 2.2$;
 $0.005 \leq Y \leq 0.012$; and
 $0.01 \leq Z \leq 0.03$.
14. A stabilized polyolefin article comprising an empirical formula, $\text{CH}_X\text{P}_Y\text{O}_Z$, where:
 $0.5 \leq X \leq 1.5$;
 $0.002 \leq Y \leq 0.05$; and
 $0.1 \leq Z \leq 0.5$.
15. The stabilized polyolefin article of claim 14, where:
 $0.617 \leq X \leq 1.245$;
 $0.004 \leq Y \leq 0.028$; and
 $0.209 \leq Z \leq 0.355$.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/047116

A. CLASSIFICATION OF SUBJECT MATTER INV. D06M11/70 D01F1/10 D01F6/04 D01F9/21 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) D06M D01F C08K		
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		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 139 476 A (HANCOCK HENRY) 13 February 1979 (1979-02-13) column 4, line 62 - column 5, line 8; claim 1 column 5, lines 26-41 -----	1-6, 12-15
X	US 2015/233021 A1 (NASKAR AMIT K [US]) 20 August 2015 (2015-08-20) paragraphs [0047], [0061], [0063], [0064]; examples 1-3 -----	7,8, 10-15
X	JP H11 171936 A (SEKISUI CHEMICAL CO LTD) 29 June 1999 (1999-06-29) abstract; examples 1-5 -----	7,10-15
E	WO 2017/167941 A1 (TOTAL RES & TECH FELUY [BE]) 5 October 2017 (2017-10-05) the whole document ----- -/--	1-15
☒ 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 "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 27 October 2017		Date of mailing of the international search report 09/11/2017
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Malik, Jan

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/047116

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	KWAN-WOO KIM ET AL: "Effects of cross-linking methods for polyethylene-based carbon fibers: review", CARBON LETTERS, vol. 16, no. 3, 15 September 2015 (2015-09-15), pages 147-170, XP055341847, ISSN: 1976-4251, DOI: 10.5714/CL.2015.16.3.147 the whole document -----	1-15

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Information on patent family members

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