Ammoxidation of polyethylene: A new route to carbon

Bryan E. Barton[*], Eric J. Hukkanen [1], Gerry F. Billovits, David Schlader, Michael J. Behr, David Yancey, Mark Rickard, XiaoHua Qiu, Daniel M. Mowery, Lora Brehm, Bryan Haskins, Weijun Wang [2], Mark S. Spalding, Chris Derstine

Core Research and Development, The Dow Chemical Company, Midland, MI 48674, United States

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A B S T R A C T

Carbon fibers boast excellent mechanical properties, but widespread adoption into everyday composite materials is limited by their high cost. Polyethylene seems like an ideal low-cost precursor based on its high carbon content, low cost, and melt-processability, but as a saturated hydrocarbon it is functionally far removed from the graphitic structure. Here, we report that after crosslinking, the oxidation of polyethylene can be performed in a controlled manner to provide significant yields of oxidized black solid that resembles its original shape and can be subsequently heated under inert atmosphere to yield a carbonaceous solid in 10–30% carbon yield. When oxidation is conducted in the presence of ammonia, nascent carboxylic acids en route to CO_2 evolution are intercepted to provide up to 70% carbon yield. This ammoxidation process was characterized by solid-state nuclear magnetic resonance, infrared spectroscopy, elemental analysis, and X-ray photoelectron spectroscopy to contain various nitrogen containing functional groups, including amides, lactams, imides, and pyridines. The resulting carbonaceous structures were characterized by Raman spectroscopy, elemental analysis, high resolution transmission electron microscope and selected area electron diffraction to be consistent with a highly disordered wavy lattice carbon structure.

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1. Introduction

At a price of $5/lb, it is envisioned that carbon fibers (CF) could enable mass adoption into the automotive, wind blade turbine, civil infrastructure, and CNG tank industries. [1–5], However, the incumbent air oxidation of poly(acrylonitrile) (PAN) fibers reaches economic parity at ca. $8–10/lb, which is governed by the precursor cost, solution-spinning limitations, conversion time, and mass yield (~50%) [6]. Polyolefins would be an excellent potential replacement precursor material for CF production due to their high carbon content, low-cost, and melt-spinability. However, the conversion of polyolefins to carbonaceous products with economically viable and scalable chemistry is a difficult challenge. A look into known stabilization chemistries of various carbon precursors teaches a

generic pathway of stabilization that involves dehydrogenation and formation of a crosslinked, extended aromatic structures [6]. Rh-catalyzed transfer dehydrogenation [7], sulfonation [8], tetra-chloroquinone dehydrogenation [9,10], air oxidative dehydrogenation [11,12], sulfur dehydrogenation [9,13,14], sulfoxidation [15–18], and halogenation/dehalogenation [19,20], are all potentially relevant chemistry options for polyethylene. However, only sulfonation, sulfur dehydrogenation, and air oxidative dehydrogenation are believed to be economically attractive. In 1969, Redfarn patented a process whereby extensively gamma-irradiated polyethylene fibers could be air stabilized to provide black fibers and subsequently carbonized at higher temperatures under an inert atmosphere [12]. Unfortunately, very little scientific analysis or analytical data was provided and there were no subsequent reports. Here, almost 50 years later, we report the first subsequent study exploring air oxidative stabilization of crosslinked polyethylene films and fibers and improvements to this generally inadequate method.

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* Corresponding author. The Dow Chemical Company, Electronic Materials, 451 Bellevue Road, Newark, DE 19713, United States.

E-mail address: bebarton@dow.com (B.E. Barton).

[1] The Dow Chemical Company, Electronic Materials, 455 Forest Street, Marlborough.

[2] Eastman Chemical Company, 200 South Wilcox Drive, Kingsport, Tennessee, 37660.

2. Experimental section

2.1. Reagents and polymers

All polymers were obtained from The Dow Chemical Company, and used as received. Ammonium hydroxide, isopropanol, xylenes, vinyl trimethoxysilane (VTMS), and Luperox 101 peroxide (2,5-bis(tert-butylperoxy)-2,5-dimethylhexane) were obtained from Sigma-Aldrich and used as received. Nacure B201 (proprietary sulfonic acid catalyst) was obtained from King Industries and used as received.

2.2. Preparation of PE-g-VTMS

PE-g-VTMS was prepared from linear low density polyethylene resin supplied by The Dow Chemical Company. The resin was an ethylene 1-octene copolymer with 0.941 g/mL and melt index of 35 dg/min (190 °C, 2.16 kg). The resin was grafted with VTMS in a co-rotating, fully intermeshing twin-screw reactive extruder by introducing the polymer, Luperox 101, and 3 wt% VTMS (VTMS:peroxide weight ratio was 80:1). The barrel temperatures were maintained at 230 °C and the screw temperature was not controlled. The extrudate temperature was typically at 240 °C. The residence time was about 3 min and upon exiting the extruder was pelletized in an underwater pelletizer. After vacuum stripping for 20 min at 140 °C, final product was characterized by NMR to contain 1.9 wt % VTMS with 65% of the VTMS units bound to the polymer chain, indicating ca. 0.6 grafts per chain.

2.3. Preparation of films and fibers

Fibers of the PE-g-VTMS resin were prepared from a commercial melt spinning line purchased from Hills, Inc. Spun fibers were ~15 μm in diameter. PE-g-VTMS films were prepared by compression molding process using a Carver Press. Typically, 0.12 g of PE-g-VTMS pellets were placed between two steel plates using PTFE liners and heated to 180 °C while applying 20,000 psig. After cooling, the plates and PTFE liner was removed to yield the desired film. Thickness was measured using a Vernier caliper thickness gauge.

2.4. Crosslinking of films and fibers

PE-g-VTMS films were crosslinked by immersion in a 5 wt% isopropanol solution of NACURE B201 (sulfonic acid catalyst sold by King Industries) for 15 h, dried in a fume hood for 24 h, and heating in a 100% relative humidity moisture oven at 60 °C for 72 h. The gel content was determined by Soxhlet extraction in refluxing Xylenes to be 69%. Thickness of the films was 0.03 in (76 μm). PE-g-VTMS fibers were crosslinked by a similar method, feeding fibers continuously into the same B201/isopropanol solution, respooling the catalyst-doped fibers, and curing the entire spool with the humid oven process above.

2.5. Oxidation and ammoxidation

In a typical oxidation or ammoxidation, 40–60 mg of VTMS-g-PE film or fibers were placed in a small quartz boat with a PTFE film liner and placed in the center of a 1″ diameter quartz tube furnace. Air flow was started through the furnace at 60 mL/min and maintained at that level throughout. The oven was ramped at 4 °C/min from ambient temperature to 260 °C and then held for 20 h. For ammoxidation, the same airflow was first directed through a glass sparging bubbler with freshly refilled ca. 200 mL of 5.0 M ammonium hydroxide maintained at ambient temperature by means of a large aluminum block bored out to mate the gas bubbler. The black film and fiber was weighed before and after oxidation. Carbonization was conducted in a similar 1″ quartz tube furnace with ~250 mL/min nitrogen flow, heated at 4 °C/min to 1000 °C. Higher temperature carbonizations were performed in a TGA apparatus.

2.6. Characterization methods

X-ray photoelectron spectroscopy (XPS) data was collected on a PHI VersaProbe II Microprobe XPS instrument with and X-ray spot size of 200 μm. Beam power was set to 50 W at 15 kV. Dual charge neutralization was used with both a low energy electron flood gun and low energy Ar$^+$ ions (7 V). A pass energy of 23.5 eV and energy step of 0.1 eV was used. The number of scans averaged for each spectral region was adjusted in order to achieve an appropriate signal to noise ratio. The data was processed and fit using CasaXPS software. For the oxidized sample, the C1s region was fit with the fewest number of Gaussian-Lorentzian components necessary in order to achieve an acceptable agreement with the data. An acceptable fit was achieved with four components that were assigned to graphitic carbon, oxygen-functionalized carbon, carboxylate groups, and a shakeup peak associated with the graphitic nature of the carbon. The peak positions from the control fibers were applied to the ammoxidized fibers, however, an additional component was necessary, and assigned as nitrogen-functionalized carbon. The N1s spectral region of the ammoxidized sample displayed an asymmetric peak shape indicating the presence of multiple nitrogen functionalities. This region was fit with three Gaussian-Lorentzian components which was the fewest necessary to achieve acceptable agreement with the data. The components were assigned to pyridinic nitrogen, amides or imides or lactams, and an ammonium species.

Raman spectra were collected with a Thermo DXR Raman microscope equipped with a 532 nm laser. The laser was focused on the sample with a 50x microscope objective, and the back-scattered light was collected with the same optics. The total acquisition time of each spectrum was 80 s.

Solid-state carbon-13 (^{13}C) NMR data were acquired at room temperature on a Bruker Avance 400 spectrometer operating at a ^{13}C resonance frequency of 100.6 MHz. Magic-angle spinning (MAS) was used at a spinning frequency of 10 kHz with a 4-mm MAS H-X-Y probe head and zirconia sample rotors with Kel-F caps. Fiber samples were firmly packed into the rotors. ^{1}H→^{13}C cross polarization (CP) was employed. Each ^{13}C{^{1}H} CP/MAS acquisition was performed with a 4-μs ^{1}H 90° excitation pulse, a 2-ms contact pulse for CP, a 5-s recycle delay, and 63-kHz TPPM decoupling during acquisition. Each 1D CP/MAS spectrum was acquired with 12 k scans. Chemical shifts were calibrated with an external standard of glycine (carbonyl, δ = 176.0 ppm). 30-Hz line broadening was used to process each spectrum.

Infrared Spectra (IR) were acquired with a Perkin Elmer Spectrum One FT-IR and Universal ATR Sampling Accessory at a resolution of 4 cm-1. Sixteen scans (~90 s acquisition time) were collected for each spectrum. The Universal ATR Accessory was equipped with a single bounce Ge crystal.

Elemental analysis was performed on a Thermo Fisher Scientific Flash 2000 Elemental Analyzer (CE Elantech, Inc). The instrument has two separate furnaces, one which is used for CHNS analysis and the other for oxygen analysis only. For CHNS analysis the samples and certified standards are weighed into tin capsules along with about 10 mg of vanadium pentoxide (V_2O_5) as a combustion aid. The samples are injected into a high temperature furnace and dosed with pure oxygen. The presence of tin in the heated, oxygen rich environment creates an exothermic reaction which temporarily increases the temperature to ensure total combustion of all