CHEMICAL DEPOLYMERIZATION OF HIGH- AND LOW-DENSITY POLYETHYLENE USING ACID TREATMENTS AND OZONATION

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PRIMARY TOPICS: Emerging Recovery and Recycling Technologies,

Building a Sustainable Circular Economy for Materials & Products

Abstract

Economic depolymerization of polyolefins is largely limited to high temperature, energy intensive pyrolysis techniques. Achieving sustainable circularity for low-cost plastics requires inexpensive processes that are not energy intensive; two such promising candidates, acid treatment and ozonation, are investigated. These approaches are being investigated to create value-added products while minimizing the generation of carbon dioxide. The acid process utilizes a mixture of acids combined with a catalyst to oxidize high-density polyethylene (HDPE) to predominantly large molecular weight dicarboxylic acid products with acid numbers and mass yields ranging between 1.0-1.2 mmol/g and 70-110% (g product/g HDPE), respectively. The catalytic ozone technique processes low-density polyethylene (LDPE) to provide water-soluble dicarboxylic acids in yields up to 15% (g product carbon/ g LDPE carbon) and insoluble material at acid numbers averaging 2.4-4.8 mmol/g. Process optimization and the use of repeated stages can improve the carbon efficiency of these processes.

Introduction and Motivation

Environmental pressures have necessitated a change in the disposable materials economy. Plastics, possessing low cost and chemical resistance, find that these same properties lead to the accumulation of solid waste in landfills and oceans. Plastics do not naturally degrade to carbon dioxide or organically processable molecules on a useful timescale; Instead, they produce micro- and nanoplastic particles which are released into water sources as an increasing serious health hazard [1]. Solutions posited to this problem consistently possess one of more of the following traits that interdict their practicality; high cost of processing, low carbon conversion efficiency, a lack of circularity, and specificity to one particular polymer while excluding others [2].

Recycling procedures (excepting reuse, landfilling, burning for energy, etc.) are broadly defined into the categories of mechanical and chemical. Mechanical recycling is the mechanical reprocessing of waste plastic into new forms. This achieves nearly perfect carbon conversion efficiency; the mechanical reprocessing continually degrades the molecular weight of the polymer, resulting in a recycled product with lower strength properties and subsequently lower value [3] [4]. Recycled plastic is often mixed with virgin material to offset this, resulting in a distinctly noncircular process. Mechanically recycling is also unable to process multilayer films or thermoset plastic [5] [6]. Chemical recycling breaks polymers down to the same chemicals extracted from crude oil that they were produced from but are plagued with high energy costs [3]. To achieve a circular economy, new and inexpensive chemical recycling processes must be developed.

Review of Related Work

Due to the relatively inert structure of PE, there is no simple chemical recycling process which converts PE back to its original monomers. This has led to the development of several chemical processes for the purpose of chemically upcycling PE to more valuable products such as precursors for polyester and acrylic [7] [8] [9] [10]. This has been investigated using various methods such as pyrolysis [11], halogenation [12], dehydration [13], hydrothermal oxidation [14] [15] [16] [17], inductive heating [18], and acid oxidation [8] [19] [20]. While many methods have shown promising results, they often required expensive catalysts, toxic solvents, and or very high operating temperatures and pressures.

A number of scientists have investigated the aqueous oxidation of polyethylene. Zawadiak et al. [21] oxidized HDPE at 120°C and 6 bar oxygen pressure and found that the presence of water reduced unwanted crosslinking reactions. Partenheimer et al. [22] investigated most common polymers under high pressure/medium temperature conditions, achieving optimal yields around 40% for polyethylene. Relatively low-pressure systems have been paired with moderate temperatures to depolymerize various grades of polyethylene in water [23] and organic solvent [15] based systems. Ozone has been used to oxidize amorphous polyethylene [24] and other saturated hydrocarbons [25] [26].

A promising approach for the upcycling of polyethylene is the use of mineral acids. Mineral acids can act as both a solvent and oxidizer and can be used effectively under less extreme conditions than most other approaches. Chlorosulfuric (CSA), fuming sulfuric (FSA), fuming nitric (FNA), and nitric (NA) acids have been used for oxidizing paraffinic materials to lower molecular weight acid products [8] [9] [19] [20]. Sulfonating acids such as CSA and FSA will sulfonate PE and require additional oxidizing treatments to achieve low molecular weight acid products [9], while FNA and NA will oxidize and depolymerize altogether [8] [19] [20]. Melby found that utilization of FNA and NA effectively depolymerizes PE to dicarboxylic acids [20]. However, in concentrated NA systems, these authors found that they would form dinitro dicarboxylic acids, which required an additional two to three chemical steps to convert them to either diketo- or pure dicarboxylic acids. For the acid treatment of HDPE shown in this work, a new single-pot-process is developed, which uses three to four times fewer process steps proposed by Melby to convert HDPE to large molecular weight dicarboxylic acids.

Technology Approach

Acid Treatment of HDPE

For the acid treatment, HDPE powder (250 μm < x ≤1.18 mm) was oxidized in a mixture of acids in the presence of catalyst under high mixing for 24 hours. The primary oxidizing acid used in this procedure was nitric acid. Using this procedure resulted in oxidation of HDPE to a fine white powder as seen in Figure 1.

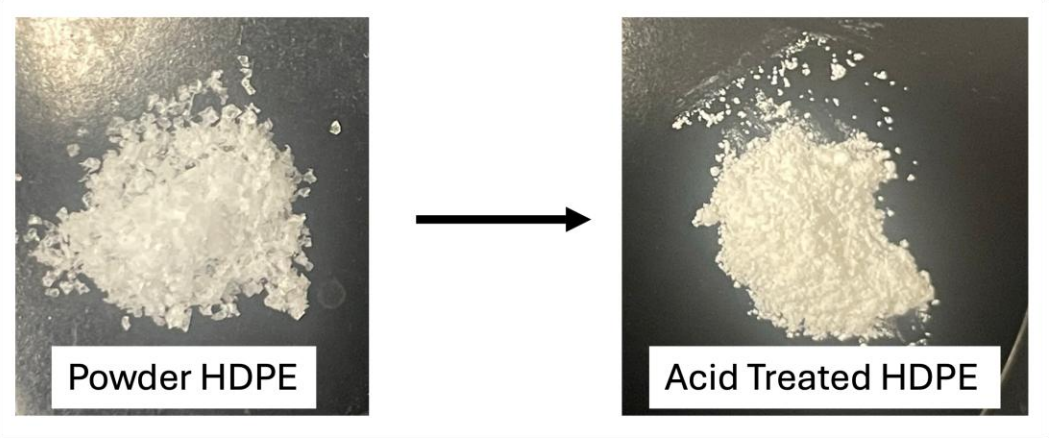

Figure 1. HDPE powder before and after acid treatment.

Ozonolysis of LDPE

LDPE powder (150 μm < x ≤250 μm) was oxidized in an ozone-sparged reactor vessel. Ozone was produced from pure oxygen using a coronal discharge ozonator. This gas stream is mixed into the liquid portion of the system in a vertical mixed-phase reactor in order to maximize solid/liquid/gas contact area and diffusion time. The waste gas stream is directed through a solution of sodium hydroxide and potassium iodide in order to strip any excess ozone. The catalyst and oxidants are able to target the C-H bonds of tertiary carbons, while leaving methylene backbone carbons mostly untouched. Over the course of the reaction, the LDPE is processed to short, linear molecules terminated in carboxylic acid groups. Once tertiary carbons have been depleted, the reaction progresses via an "unzipping" reaction from a carboxyl radical, leading to a reduction in the molecular weight of the polymer concomitantly with the production of low-molecular weight dicarboxylic acids, which are somewhat resistant to further oxidation in the system.

Characterizations

Acid Number Titrations. Acid titrations were performed using standardized 0.05 M KOH in ethanol and xylene following dissolution of at least 0.5 g of product in xylene near the reflux temperature using phenolphthalein as an indicator [20]. The titrant was standardized by titration of 99% adipic acid dissolved in methanol.

Fourier Transform Infrared Attenuated Total Reflectance (FTIR-ATR) Spectroscopy. FTIR-ATR was conducted on a Thermo Scientific Nicolet™ iS50 Fourier Transform Infrared Spectrometer using a 32 scans at a resolution of 2 cm^{-1}. The diamond interface was washed with isopropanol between each scan.

Nuclear Magnetic Resonance (NMR) Spectroscopy. NMR was conducted using a 20% product/ 80% solvent ratio. The solvent used was 0.05 M Chromium Acetylacetonate in 1,2,4 trichlorobenzene at 120°C.

Discussion

Acid Treated HDPE

Acid treatment of HDPE in a mixture of acids and catalyst proved to be a highly tunable reaction process. Across a number of trials varying the quantity of catalytic species, temperature, and time of the reaction, resulted in solid mass yields (g of product/g of HDPE) and acid numbers of approximately 40 to 110% and 1.0 to 2.6 mmol/g, respectively. In general, it was found that the addition of catalytic species up to certain mass percents resulted in faster reactions and increased the solid mass yield while simultaneously increasing species acid number. In contrast, increasing reaction temperatures gave products with higher acid numbers, but lower mass yields. These observations indicate that moderate reaction temperatures with catalyst should help increase reaction efficiency and mass yield.

To understand the underlying chemical composition of acid treated HDPE using FTIR-ATR, a portion of titrated products with an acid number of 1.2 mmol/g and mass yield of 70% were reacidified using hot aqueous sulfuric acid. All products from each of these steps (Acid, titrated, titrated-acid washed), after being rinsed, filtered, and dried, were taken and analyzed using FTIR-ATR. The absorbance of these various products between 1500 and 1800 cm^{-1} are shown in Figure 2. As can be seen, the original acid product in the carbonyl region around 1700 cm^{-1} shows what could be approximately three peaks around 1730, 1710, and 1698 cm^{-1}, whereas the small peak around 1550 cm^{-1} indicates residual secondary NO_2 groups added during the oxidation with nitric acid. The carbonyl peaks could indicate that in addition to carboxylic acids being present, there could also be esters and ketones. However, following the titration of acid treated HDPE products, the carbonyl peaks completely shifted to form a large characteristic carboxylate peak overlapping with NO_2 absorbance around 1570 cm^{-1} [27]. The absence of a carbonyl peak around 1700 cm^{-1} for the titrated products is strong evidence that no ketones are present in the acid treated material. Similarly, the products of the titrated-acid washed products showed a very similar spectrum compared to the original acid product; indicating that esters are unlikely present, since they would have been converted to carboxylates and carboxylic acids following the titration and reacidification, respectively. The dominance of carboxylic acids over all other groups was further evidenced by the total absorbance ratios between 1500 and 1800 cm^{-1} of the titrated and titrated-acid washed products relative to the original acid product maintaining a value around 1. Given these products are strictly dicarboxylic acids with minimal additional functionality, the three peaks could indicate three different COOH interactions present within the chains such as isolated [28], amorphous, and crystalline groups. Based on these results, the range of molecular weights and carbon numbers would be somewhere around 769 to 2000 g/mol and 58 to 161.

This catalyzed mixed acid system presents a more efficient way of converting HDPE to dicarboxylic acids in high yield using a one-pot-process. The dicarboxylic acid products can be converted to greases/waxes, further decomposed to lower molecular weight products, and repolymerized to form polyesters. Ongoing work is investigating additional depolymerization pathways to fine tune product distributions.

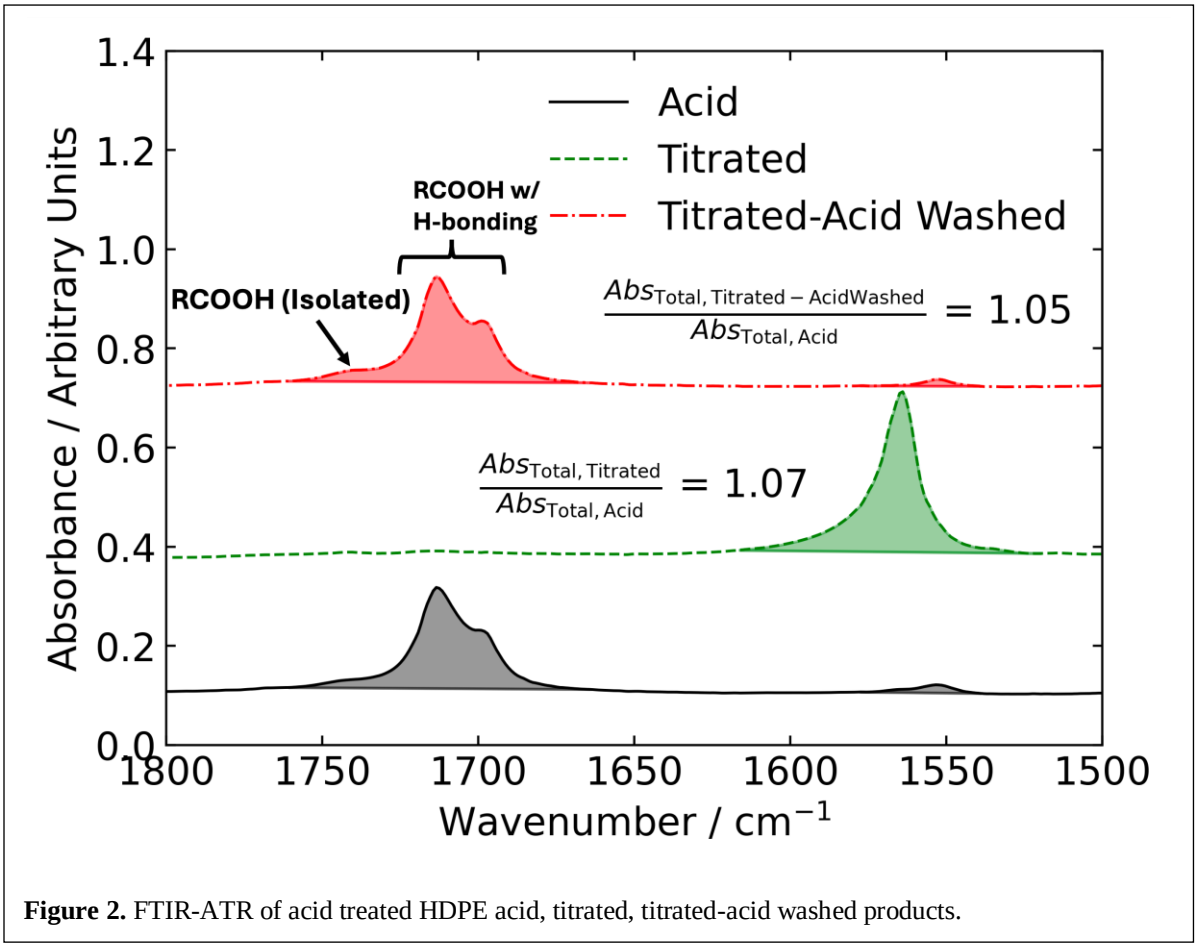

Figure 2. FTIR-ATR of acid treated HDPE acid, titrated, titrated-acid washed products.

Ozonolysis of LDPE

Samples were extracted once every 24 hours for a 144 hour period. Solid products were examined by ATR-IR and NMR spectroscopy.

Figure 3 shows the terminology for NMR analysis peak associations. The α and β designate methylene groups from functionalization or a branch point if unspecified. Terminology is adapted with some changes from Galland et al [29].

Figure 4 shows the complete NMR spectra for the solid samples. The emergence of peaks at 207 and 177 PPM correspond to ketone and carboxylic acid/ester signals, respectively. The joint carboxylic acid/ester peak can be deconvoluted in IR. The large peak between 120 and 140 PPM is due to solvent signal. The range between 50 and 0 PPM, however, contains signals for methylene peaks, including those α- or β- to branch points or functionalization. This range is examined closer in figures 2-5.

Figure 5A shows the range of 50-32 PPM for the NMR section containing methylene signals. The peak at 43.75 is a strong new signal not seen in the virgin material and is likely the α-ketone atom. Peaks at 38 and 40 ppm, corresponding to Et and Bu/Am/L branch points, respectively, are nearly extinguished. The peak at 34.5 ppm, representing the α-branch methylene, is likewise extinguished with a distinctly new peak emerging at 34 ppm. The gradual shift to this new peak is also visible in Figure 6A. Figure 5B shows the range of 32-9 ppm; the peak associated with β-branch points at 26.25 ppm shows similar behavior to the α-branch peak at 34.5 ppm. Figure 3 shows the signal changes over the first 48 hours of oxidation; the gradual reduction of the α- and β-branch points is clearly displayed. Figure 6B shows the effect of oxidation on methyl peaks; while tertiary carbon signals are almost completely eliminated, some Bu/Am/L branch methyl groups remain. Shorter chain methyl groups, seen at 11 (ethyl C1) and 8 (possibly methyl C1) ppm are completely removed

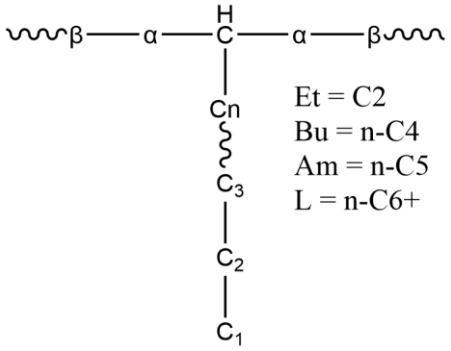

Figure 3. Key for terminology in figures 2-5. Propyl and methyl branches are rare. *n*-butyl branches are 5-15 times more common than other short branches, and 20-50 times more common than long branches [31]. LDPE peak assignments from Galland et al. [29]

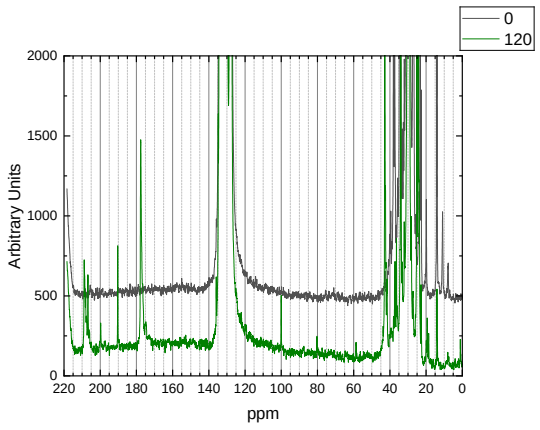

Figure 4. Complete ^{13}C NMR of virgin and 120 hour oxidized LDPE. Carboxylic acid signals are visible at 177 ppm. Ketone signals are visible at 209 ppm

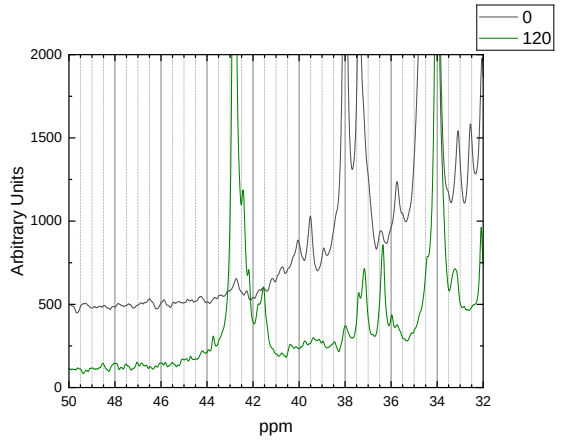

Figure 5A. ^{13}C NMR of the range 50-32 ppm, showing peaks for α-ketone (42.75), branch-Et (40), branch-Bu,Am,L (38), α-branch (34.5), α-carboxylic acid (34)

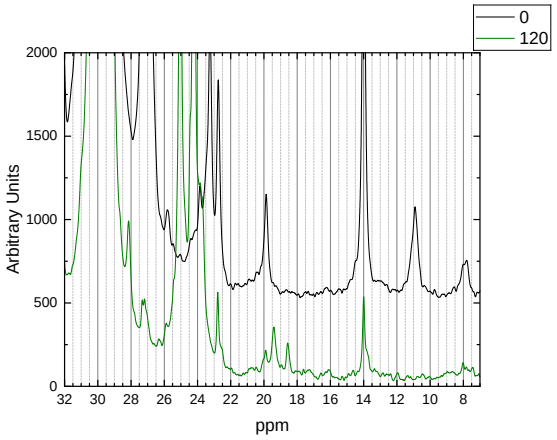

Figure 5B. ^{13}C NMR of the range 32-7 ppm showing peaks for backbone CH_2 (30), β-branch (27.5), β-ketone/carboxylic acid (25 and 24.25), C2-Bu (23.25), C2-Am/L (22.75), C1-Bu/Am/L (14), C1-Et (11)

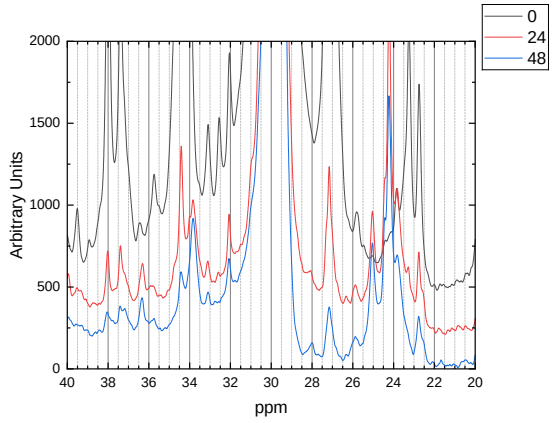

Figure 6A. ^{13}C NMR of the range 40-20 ppm, showing the decaying signal from α (34.5) and β (27.5) carbons over the first 48 hours of oxidation

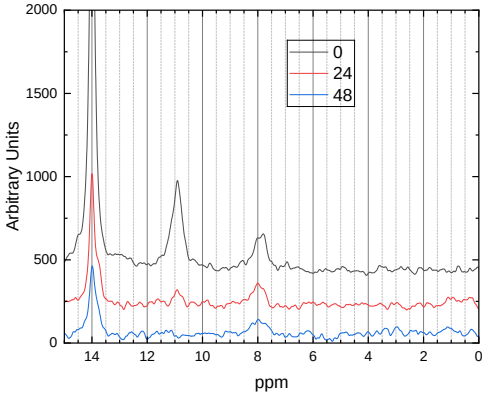

Figure 6B. ^{13}C NMR of the range 15-0 ppm showing the decaying signal from C1-Bu/Am/L (14) and C1-Et (11) peaks over the first 48 hours of oxidation

.Over the course of the 120 hour oxidation period, a simplification in the number of peaks shown in NMR indicates a reduction in the diversity of different secondary carbons. Tertiary carbons are almost completely removed, while primary carbons show a huge reduction in signal. This indicates that tertiary carbons are selectively digested to produce a difunctionalized chain scission point. The produced linear material is presumably of a length similar to the distance between branch points, roughly 40-125 carbons in length.

Conclusions and Recommendations

High and low density polyethylenes were successfully degraded to diacids under mild conditions. Disenthralling chemical recycling systems from high temperatures saves energy and allows the reaction to be carried out in less expensive equipment. Specifically targeting C-H bonds allows for these processes to accept most plastic types including multilayer films. The use of water and mineral acid chemistry removes the need for organic solvents that can be environmental or health hazards. While the solid-state chemical processing of LDPE and HDPE is shown to be effective, further work must be done to determine if these systems are economically efficient.

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