Oxyfunctionalization of polymers: a mass transport problem

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Highlights

- Expanded bed reactor allow 20x oxyfunctionalization.
- Gas, liquid and solid characterization achieved for HDPE samples.
- Batch and extrusion comparisons display strong mass transfer limitations.

1. Introduction

Oxyfunctionalization of polyethylene (PE) alters the polymer surface properties, making polymers more compatible with polar environments. Direct oxidative PE upgrading is a promising technology, but most reported systems are mass transfer limited or rely on thin films to enable oxidation. Here we report on the use of expanded-bed reactor architecture to overcome mass transfer constraints, enabling up to 20× higher oxyfunctionalization of High-Density Polyethylene (HDPE), relative to reactive extrusion or conventional batch processing.

2. Methods

Comprehensive fractionation and analysis of solids, liquids, and gases (using Nuclear Magnetic Resonance, Gas Chromatography, Gel Permeation Chromatography, and Fourier Transform Infrared Spectroscopy) reveals a distribution of oxygenated functionalities (ketones, alcohols, esters, carboxylic acids, lactones, and aldehydes). The experimental work was performed in a modular laboratory-scale reactor. Air was fed upstream across the reactor of 3 cm of internal diameter and 50 cm of length. The bed was filled with 10 g of high-density polyethylene pellets (Marlex 9012 HDPE Mw= 62 kDa) which were mixed with 25 g of 2 mm SiC chips (Advance Ceramic Materials GmbH (ACM)). The bed was held by glass frits, used as a distribution plate. A condenser, set to -4 °C, was placed at the reactor outlet, where the gas and the liquid phases were separated in a 50 mL three-neck round bottom flask operating under atmospheric conditions. The precise reactor operating conditions allow control over both the average molecular weight and the extent of oxidation.

3. Results and discussion

The extent of oxidation and the percentage of each functional group observed in Figure 1 represents the solid phase remaining in the reactor. Therefore, this linear trend shown in Figure 1c does not include oxygen functionalities presented in the gas or liquid phase. The functional group distributions shown in Figure 1d illustrate that the functional groups present in the oxidized polymer remain similar between 175 ºC and 300 ºC, with carboxylic acids and alcohols being the most abundant functional groups. This suggests that although there is some crosslinking present at 125°C, but as this temperature is exceeded, more chain scission and less crosslinking is present, which correlates clearly with the decrease in the molecular weight and the increase in the appearance of the gas-phase products (Figure 1a and Figure 1b). Interestingly, 150 ºC is the onset of temperatures screened beyond the melt temperature of the HDPE utilized (~136 ºC).

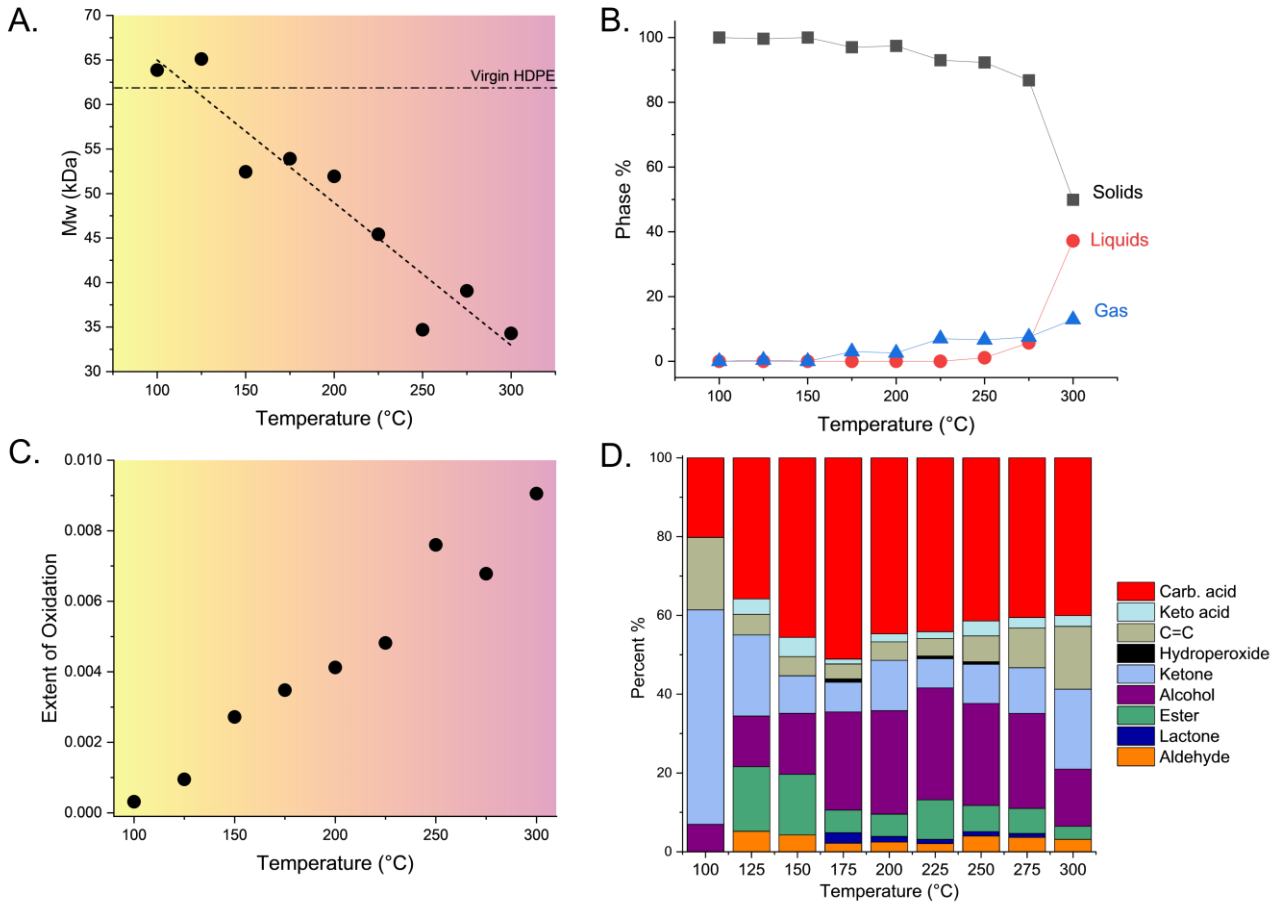

Figure 6. Temperature effect on HDPE autoxidation, A) molecular weight of the collected product polymer, B) phase distribution of the obtained product, C) extent of oxidation of the solid fraction and D) percentage of functional groups in the product polymer.

The liquid and gas fractions from these experiments were analyzed, too. NMR revealed that the liquid fractions were comprised of mostly the same functional groups as the polymer. When larger quantities of liquid sample were produced, such as in oxidations at 275 °C and higher temperatures, two layers of liquid material were observed. A more wax-like fraction and a liquid portion were produced likely due to differences in the molecular weight. Because of these differences in the chain length, different NMR solvents had to be used. We can observe from the liquid fraction NMR analysis a clear indication of carboxylic acids, ketones, and alcohols, esters, aldehydes, lactones, hydroperoxides, keto acids, diketones, and carbon-carbon double bonds a similar function group distribution to the solids but a lower molecular weight. The gas fraction for most of these samples were composed of air due to the high flow needed to achieve the bed expansion. Low concentrations of carbon monoxide and carbon dioxide were observed as well.

4. Conclusions

We demonstrate that an expanded-bed reactor can alleviate both constraints simultaneously. Relative to extrusion, the expanded bed produces ~20× higher total oxidation, enabling as high as ~2.5 oxygenated functional groups per chain.

Keywords – Expanded bed reactor, polymer oxidation, reactive extrusion and batch.