Introduction

Polyolefins or polyalkenes are a class of polymers extensively used in the industry because of its characteristics that depend on the arrangement of their ethylene in crystalline form (high density polyolefin “LDPE”) or amorphous (low density polyolefin “LDPE”).

New analytical pyrolysis hyphenized techniques can provide valuable information (processes, origin and fingerprinting) about natural and synthetic polymers. In this communication the chemical structure of a low-density green polyethylene and a high-density white polyethylene were studied in detail using conventional micro-furnace analytical pyrolysis, bulk stable isotopic analysis and pyrolysis released compound specific stable isotopic analysis.

Methods

Pyrolysis-gas chromatography–mass spectrometry (Py-GC/MS) was performed for polymer characterization using a double-shot pyrolyzer (Frontier Laboratories, model 2020) attached to a GCMS system Agilent 6890N. Compound assignment was achieved via single-ion monitoring for various homologous series, via low-resolution mass spectrometry, and comparison with published and stored (NIST and Wiley libraries) data. Bulk isotopic signature of light elements (δ13C, δ15N, δ18O, δD) was obtained using a Flash 2000 HT (N, C, S, H and O) elemental analyzer EA1112 coupled to a Delta V Advantage IRMS (Thermo Scientific) (IRMS).

Compound specific isotope analysis (CSIA) of stable light elements C, N, and H was measured directly in the pyrolysis products from the plastic (Py-GC-(FID)-CTC-IRMS). This was done by coupling a pyrolysis unit (double-shot pyrolyzer Frontier Laboratories, model 3010D) to a gas chromatograph fitted with a flame ionization detector (GC/FID) and coupled to the Delta V Advantage IRMS through a GC-isokin System (Thermo Scientific) capable of both combustion (C) and high temperature pyrolysis (TC) (Py-GC-(FID)-CTC-IRMS). Isotopic ratios are reported as parts per thousand (%‰) deviations from appropriate standards recognized by the international atomic energy agency (IAEA).

Results and Discussion

Analytical pyrolysis (Py-GC/MS): a series of n-alkane, α-alkene and α,ω-diene (C8 to C37 chain length) were released in each polyethylene (white and green). A peak at c. min. 6 was identified as α-Chloroaniline (1-Amino-2-chlorobenzene) corresponding to the plastic’s green dye (fig. 4C).

Bulk isotopic analysis (TCEA-IRMS): the values obtained for the whole white polymer were δD= -102.1±0.4 ‰, δ13C=79.2±0.3 ‰. δ18O= ±15.3±0.6 ‰. δD was not detected due to the low signal contribution from the solvent.

Compound specific isotopic analysis (Py-GC-(FID)-CTC-IRMS): For the green polyethylene plastic, the carbon isotopic signature was similar δC (-30.1±0.6 ‰) for the three homologous series resolved (α,ω-diene -29.5±0.7 ‰; α-alkene -29.9±0.4 ‰; n-alkane -30.3±0.5 ‰) different from that of the green dye (α-Chloroaniline) (-27.1±0.6 ‰). This was the only N bearing structure and δ15N was obtained (>+21.9±2.0 ‰). These signatures are in line with tabulated values for synthetic materials and also indicate that polyethylene and dye are probably from a distinct origin (Fig. 4A). No C data is available for the white polymer.

In the range where it was possible to unambiguously measure isotope ratio (Work area: no-coelution zone between C12 and C19), significant differences were observed in the average compound specific δD values for the three structures for each polyethylene sample; Low-density polymer: α,ω-diene -67.4±3.0 ‰; α-alkene -74.7±1.5 ‰, n-alkane -75.9±5.4 ‰. High-density polymer: α,ω-diene -80.2±3.3 ‰, α-alkene -100.9±5.3 ‰, n-alkane -115.3±3.2 ‰.

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