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A multidimensional fractionation protocol for the oligomer analysis of oxidized waxes

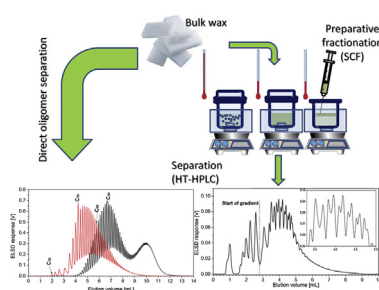
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HIGHLIGHTS

- High-temperature HPLC separation of oxidized and non-oxidized waxes on PGC is investigated for the first time.
- Separation of oxidized and non-oxidized polyethylene waxes is optimized and adapted for use in comprehensive HT-2D-LC.
- The solution crystallization process is used to obtain narrow wax fractions for analysis using advanced analytical methods.

GRAPHICAL ABSTRACT



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ABSTRACT

Oxidized waxes possess far superior properties as compared to the alkanes they are derived from. The separation of alkane oligomers via gas chromatography (GC) becomes a challenge when polar oxygen-containing functional groups are introduced or when higher molar masses are targeted. In the present study, the separation and analysis of oligomers in oxidized and non-oxidized waxes using different liquid chromatographic techniques are investigated. Oligomers in two oxidized waxes and a non-oxidized wax from which they are derived, are separated using high-temperature solvent gradient interaction chromatography (HT-SGIC) and high-temperature two-dimensional liquid chromatography (HT-2D-LC). Evaporative light scattering detector conditions are tailored to provide the best detection with the solvent system at use. It is shown that oligomers in oxidized and non-oxidized waxes can be separated and identified using the mentioned techniques. It has been found that the ELSD detector response systematically decreases as the oxidation levels of the waxes increase. Coupling of HT-HPLC and high-temperature size exclusion chromatography (HT-SEC) in a comprehensive 2D-LC setup shows a broadening of the molar mass distributions of the lower oligomer fractions as a consequence of the modification indicating changes in the oligomer chain microstructures. A preparative fractionation technique is utilized to collect specific oligomer fractions from the bulk waxes followed by hyphenation to HT-HPLC and other techniques. HPLC is shown to provide more detailed information on the oligomer composition of waxes when coupled to a pre-fractionation technique.

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1. Introduction

When alkanes/ethylene oligomers are oxidized or modified to introduce oxygen functionalities, the majority of their physical and mechanical properties are significantly improved. This expands

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their areas of application including solubility in polar media, compatibility with polar organic/inorganic materials and better adhesion [1–3]. The latter is crucial when waxes are used as coatings in food and packaging as migration into food is reduced. Industrially fabricated waxes are usually a mixture of a wide range of oligomers and in some cases, small amounts of high density polyethylene (HDPE). The oxidation of waxes is typically done by bubbling oxygen or oxygen containing gases through molten wax [4]. Reaction conditions can vary depending on the degree of oxidation required for the end product. Deckers et al. [2] oxidized wax at 160 °C whereby a steel autoclave with pressure maintenance device was used. Molten wax is stirred continuously while air bubbled at the desired flow rate. Gas chromatography (GC) has been the main workhorse in the separation and identification of olefin oligomers [5–9] due to its outstanding peak resolution and selectivity. However, GC has distinct limitations when separating alkanes of 30 or more carbons. The incorporation of oxygen functionalities increases the wax vaporisation temperatures and hence it requires higher GC operational temperatures. Furthermore, even when higher operation temperatures are employed, peak resolution of higher oligomers (90–100 carbons) is lost.

Liquid chromatography (LC) offers an alternative route for the separation and identification of wax oligomers. Of the several modes of operation available in liquid chromatography, size exclusion chromatography (SEC) has been largely employed to separate wax/oligomer macromolecules [10–12]. The technique has been preferred due to its rapid nature and possibility of functional group determination when coupled to infrared spectroscopy online or offline. However, the technique does not provide sufficient resolution to separate individual oligomers in a single experiment. There have been several attempts to separate oligomers using stationary phases with small pores. Oligomers with 5–150 carbon atoms have been separated with silica gel and porous glass [11,13–17] being used as stationary phases for SEC separations.

Separations based on adsorptive interactions have been investigated using weak eluents and at ambient temperatures to promote adsorption onto silica gel, alumina, or zeolites which were employed as stationary phases [18–23]. The development of high temperature liquid chromatography by Macko and Pasch [24–27] brought new possibilities in the separation and identification of complex components in polyolefins with high molar masses. Porous graphitic carbon (PGC, e.g. Hypercarb[®]) has been repeatedly shown to separate ethylene-based polyolefins according to the number of linear methylene sequences in a given polymer chain [28–31]. Möckel et al. [32] demonstrated the ability of porous graphitic carbon to have stronger retention of oligomers with 6–15 carbon atoms as compared to silica gel C18 with methanol as the eluent. Recently, Mekap et al. [33] separated oligomers present in low molar mass linear high density polyethylene (HDPE) standards with almost baseline resolution on Hypercarb[®]. This has been an important starting point, demonstrating the ability of HT-HPLC to separate a wide range of oligomers with high precision. The presence of the functional groups has not been shown to influence the separations on the Hypercarb[®]. On the other hand, the detector response has been shown to change when functional groups have been introduced in polyolefin polymer chains [34–36].

Fractionation of bulk materials (e.g. polyolefins) into homogeneous fractions by chemical composition/branching or molar mass has been shown to greatly aid the complete unravelling of polyolefin microstructures [37–43]. Preparative temperature rising elution fractionation (p-TREF) [30,40,43–47], solution crystallisation fractionation (SCF) [48], and preparative molar mass fractionation (p-MMF) [47,49] have been presented as important and indispensable tools for the fractionation of semicrystalline

polyolefins by chemical composition or molar mass. Hyphenation of these techniques to other new chromatographic techniques provides a wealth of information especially when coupled to information-rich detectors. Applying these techniques to low molar mass waxes presents a challenge especially when oxidized functionalities are introduced. This is due to the changes in solubility of the waxes in the solvents used for fractionation at ambient temperatures.

In the present study, we investigate the oligomer separation, selectivity and retention behaviour of non-oxidized and oxidized waxes on PGC using solvent gradients and isocratic solvent techniques. A suitable preparative technique is employed in the fractionation of the bulk waxes. A combination of separations in the first dimension (on PGC) to separations according to size (HT-SEC) in tailored comprehensive high-temperature two-dimensional liquid chromatography (HT-2D-LC) experiments is presented and discussed.

2. Experimental

2.1. Samples and solvents

Three waxes (designated as No. 1, No. 2 and No. 3) were used for the present study. Wax No. 1 is the starting material obtained from Sigma Aldrich, South Africa, from which oxidized waxes No. 2 and No. 3 were derived by passing oxygen through a melt of wax No. 1 for different times. Ethylene oligomers C₁₈ - C₅₀ were purchased from Sigma-Aldrich, South Africa, and the C₄₀ as well as the C₅₀ standards were used for SEC calibration. High density polyethylene standards (1, 2, 33 and 55 kg mol⁻¹) were obtained from Polymer Standards Service, Mainz, Germany. Narrowly distributed polystyrene standards used for SEC calibration were obtained from Agilent Technologies, UK.

1,2,4-trichlorobenzene (TCB) was used for size exclusion chromatography. *n*-Decane and 1,2-dichlorobenzene (ODCB) of HPLC grade were used for solvent gradient experiments. *n*-Heptane was used for isocratic experiments. The solvents were obtained from Sigma-Aldrich, South Africa and were used as received.

2.2. Size exclusion chromatography (SEC)

Molar mass and molar mass dispersity values were determined on a PL-GPC 220 High Temperature Chromatograph [Polymer Laboratories, Church Stretton, UK (now Agilent)] equipped with a differential refractive index (RI) detector. The samples (4 mg) were dissolved in 2 mL of TCB for 0.5 h together with 0.025% BHT which acted as a stabiliser to prevent sample decomposition/degradation. TCB with 0.0125% BHT was the mobile phase at a flow rate of 1 mL min⁻¹. Three 300 × 7.5 mm² PLgel Olexis columns (Agilent Technologies, UK) were used together with a 50 × 7.5 mm² PLgel Olexis guard column and 200 μL of each sample was injected. All experiments were carried out at 150 °C. The instrument was calibrated using narrowly distributed polystyrene standards as well as narrowly distributed polyethylene standards (Table 1s). The Cirrus GPC Version 3.3 (Polymer Laboratories) was used for data acquisition and evaluation.

2.3. Fourier transform infrared spectroscopy (FTIR)

Attenuated total reflectance (ATR) measurements were recorded on a Thermo Nicolet iS10 spectrometer. Solid samples were used in all the analyses with no prior modifications (except drying in the case of fractions). Spectra recorded from 4000 to 650 cm⁻¹ were obtained from a collection of 64 scans at a resolution of 4 cm⁻¹ with automatic background subtraction. Thermo Scientific

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