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## APPENDIX A: PUBLICATIONS

### JOURNAL ARTICLES

Phillips, J., Weldhagen, M., **Mhlabeni, T.**, Radebe, L., Ramjee, S., Wesley-Smith, J., Atanasova, M. & Focke, W. W. 2021. Thermal characterisation of metal stearate lubricant mixtures for polymer compounding applications. *Thermochimica Acta*, 699, 178906.

**Mhlabeni, T.**, Ngobese, C., Ramjee, S., & Focke, W. W. 2023. Rheological characterisation of linear low-density polyethylene–Fischer–Tropsch wax blends. *Journal of Vinyl & Additive Technology*, 1.

**Mhlabeni, T.**, Ramjee, S., López, J., Díaz-Díaz, A.-M., Artiaga, R. & Focke, W. 2023. Thermal and rheological properties of Fischer–Tropsch wax/high-flow LLDPE blends. *Macromolecular Materials and Engineering*, n/a, 2300125.

## APPENDIX B: MATERIAL DATA SHEET

### WAX RESINS DATA SHEET

Referred to as L-WAX in text



#### *product data sheet*

#### **Sasolwax M3B**

Code 1388    Revision 4    31 May 2018

<b>Properties</b>	<b>Test method</b>	<b>Units</b>	<b>Specification</b>	<b>Typical values</b>
<i>Congealing point</i>	<i>ASTM D 938</i>	<i>°C</i>	<i>58 - 64</i>	<i>62</i>
<i>Penetration at 25°C</i>	<i>ASTM D1321</i>	<i>0.1 mm</i>	<i>17 - 23</i>	<i>20</i>
<i>Oil Content</i>	<i>ASTM D721</i>	<i>mass %</i>	<i>4.2 max</i>	<i>3.8</i>
<i>Colour</i>	<i>Sasol 2000</i>	<i>Saybolt</i>	<i>+ 17min</i>	<i>+27</i>
<i>Appearance</i>	<i>Sasol 1074</i>	<i>-</i>	<i>Clear at 90°C</i>	<i>Clear</i>
<i>Water crackle test</i>	<i>Sasol 1087</i>	<i>-</i>	<i>Pass splutter test</i>	<i>Pass</i>
<i>Centrifuge test</i>	<i>Sasol 1052</i>	<i>-</i>	<i>Free from foreign material</i>	<i>Pass</i>

#### **Packaging**

*Sasolwax M3B is supplied as Liquid, pastilles or powder in 20kg polyethylenen bags or in boxes as 25kg slabs.*

#### **Note**

*To obtain the best performance from the product, we recommend use within 5 years from sample date on the Certificate of Analysis. Product should be stored under standard warehousing conditions, at least in a clean dry place, in its original packing at a temperature not exceeding 35°C*

#### **Notice**

***This product information is indicative and does not include any guarantee***

**Sasol Chemicals a division of Sasol South Africa (Pty) Ltd.  
ISO 9001/ISO 14001**

Referred to as H-WAX in text



## product data sheet

### Sasolwax H1

Code 1550 Revision 18 27 March 2019

Properties	Test method	Units	Specification	Typical values
Congealing point	ASTM D 938	°C	96-100	97
Drop melting point	ASTM D 3954	°C	-	112
Penetration at 25°C	ASTM D 1321	0.1 mm	1 max	1
Penetration at 65°C	ASTM D 1321	0.1 mm	20 max	18
Acid Value	ASTM D 1386/7	mg KOH/g	-	<0.1
Saponification value	ASTM D 1386/7	mg KOH/g	-	<0.5
Brookfield viscosity at 135°C	Sasol 1010	cP	6-10	8
Bromine value	Sasol 3016	g Br/100g	-	0.1
Colour	Sasol 2000	Saybolt	+15 min	+22
Oil content	ASTM D 721	mass %	-	0.2
MIBK solubles	Sasol 4036	mass %	1.5 max	0.8
Centrifuge test	Sasol 1052		Free from foreign material	Pass
Molecular weight	-	Dalton	-	880
UV absorptivity @290 nm	ASTM D2008-12	L/g.cm	-	<0.01

#### Compliance

##### F&DA

This product complies with the requirements of 21 Code of Federal Regulations: Parts 172.615 (Chewing gum base), 175.105 (Adhesives), 175.250 (Paraffin, synthetic), 175.125 (Pressure sensitive adhesive), 175.300 (Resinous & Polymeric coatings), 175.320 (Resinous & Polymeric coatings for Film), 176.170 (Components of Paper & Paperboard, Wet), 176.180 (Components of Paper & Paperboard, Dry), 177.1200 (Cellophane), 177.1390 (Laminate Structures) and 177.1210 (Closures with sealing gaskets for food containers).

BfR recommendation: This product complies with BfR requirement XXV, Part C, (Synthetische Hartparaffine)

#### Packaging

Sasolwax H1 is supplied in the form of pastilles packed in 20kg paper bags and 700kg and coarse powder packed in 20kg paper bags or 600kg.

#### Note

To obtain the best performance from the product, we recommend use within 20 years from sample date on the Certificate of Analysis. Product should be stored under standard warehousing conditions, at least in a clean dry place, in its original packing at a temperature not exceeding 35°C.

**Notice** This product information is indicative and does not include any guarantee

Sasol Chemicals a division of Sasol South Africa (Pty) Ltd.  
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# POLYMER RESIN DATA SHEET

Referred to as L-LLDPE in text



**SABIC® LLDPE M500026**  
 Linear low density polyethylene for masterbatch compounding

**Description**

SABIC® LLDPE M500026 is a high flow linear low density polyethylene copolymer grade with a narrow molecular weight distribution.

**Application**

SABIC® LLDPE M500026 resin is recommended for injection moulding masterbatch where a high filler acceptance is required, combined with a good flow.

**Processing conditions**

Typical moulding conditions for SABIC® LLDPE M500026 are: material temperature 180 - 230 °C (355 - 450 °F).

**Mechanical properties**

Test specimen is prepared from compression moulded sheet made according to ASTM D-1928, procedure C.

**Typical data.**

Revision 20060418

Properties	Units SI	Values	Test methods
<b>Polymer properties</b>			
<b>Melt flow rate (MFR)</b> at 190 °C and 2.16 kg	g/10 min	<b>50</b>	ASTM D 1238
<b>Density</b>	kg/m <sup>3</sup>	<b>926</b>	ASTM D 1505
<b>Mechanical properties</b>			
<b>Tensile test</b>			ASTM D 638
stress at yield	MPa	<b>13</b>	
stress at break	MPa	<b>12.4</b>	
strain at break	%	<b>120</b>	
secant modulus at 1% elongation	MPa	<b>354</b>	
<b>Izod impact notched at 23 °C</b>	J/m	<b>450</b>	ASTM D 256
<b>Hardness Shore D</b>	-	<b>55</b>	ASTM D 2240
<b>ESCR</b>	h	<b>2</b>	ASTM D 1693
<b>Thermal properties</b>			
<b>Vicat softening temperature</b> at 10 N (VST/A)	°C	<b>88</b>	ASTM D 1525
<b>Brittleness temperature</b>	°C	<b>&lt;-75</b>	ASTM D 746

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## SABIC® LLDPE M50026

### Linear low density polyethylene for masterbatch compounding

**General information.** SABIC® LLDPE grades are available in a wide range of viscosities. Supplementary to this, various grades are also available in powder form. This unique combination makes SABIC® LLDPE grades extremely suitable for masterbatch and compounding applications.

The SABIC® LLDPE portfolio offers an excellent choice to find a good base resin for both additives, black, white and colour masterbatches, with varying amounts of additives and pigments.

**Health, Safety and Food Contact regulations.** Detailed information is provided in the relevant Material Safety Datasheet and or Standard Food Declaration, available on the Internet ([www.SABIC-europe.com](http://www.SABIC-europe.com)). Additional specific information can be requested via your local Sales Office.

**Quality.** SABIC Europe is fully certified in accordance with the internationally accepted quality standard ISO 9001-2000. It is SABIC Europe's policy to supply materials that meet customers specifications and needs and to keep up its reputation as a pre-eminent, reliable supplier of e.g. polyethylenes.

**Storage and handling.** Polyethylenes resins (in pelletised or powder form) should be stored in such a way that it prevents exposure to direct sunlight and/or heat, as this may lead to quality deterioration. The storage location should also be dry, dust free and the ambient temperature should not exceed 50 °C. Not complying with these precautionary measures can lead to a degradation of the product which can result in colour changes, bad smell and inadequate product performance. It is also advisable to process polyethylene resins (in pelletised or powder form) within 6 months after delivery, this because also excessive aging of polyethylene can lead to a deterioration in quality.

**Environment and recycling.** The environmental aspects of any packaging material do not only imply waste issues but have to be considered in relation with the use of natural resources, the preservations of foodstuffs, etc. SABIC Europe considers polyethylene to be an environmentally efficient packaging material. Its low specific energy consumption and insignificant emissions to air and water designate polyethylene as the ecological alternative in comparison with the traditional packaging materials. Recycling of packaging materials is supported by SABIC Europe whenever ecological and social benefits are achieved and where a social infrastructure for selective collecting and sorting of packaging is fostered. Whenever 'thermal' recycling of packaging (i.e. incineration with energy recovery) is carried out, polyethylene -with its fairly simple molecular structure and low amount of additives- is considered to be a trouble-free fuel.

Internet [www.SABIC-europe.com](http://www.SABIC-europe.com)  
email [TCC.TM-PE@SABIC-europe.com](mailto:TCC.TM-PE@SABIC-europe.com)

Referred to as H-LLDPE in text

## PRODUCT DATA SHEET



LLDPE	LLDPE	LLDPE	LLDPE	LLDPE	LLDPE	LLDPE	LLDPE	LLDPE	LLDPE			
<b>Linear Low Density Polyethylene</b>					<b>HM2420</b>		<b>Technical support:</b> Polymer Technology Services Centre 22 Pressburg Road, Modderfontein, 1645 South Africa  Tel: +27 (0)11 458 0700 Fax: +27 (0)11 458 0734			<b>Sales office:</b> Sasol Base Chemicals PO Box 5486 Johannesburg, 2000 South Africa  Tel: +27 (0) 10 344 5000 polymers@sasol.com		

Date of issue: March 2017

www.sasol.com

**Melt Index: 20 g/10min**

**Density: 0.924 g/cm<sup>3</sup>**

### Features

- High gloss
- Excellent low temperature impact strength
- Good ESCR
- Hexene copolymer

### Applications

- Injection moulded containers and lids
- Base polymer for masterbatch

### Additives

- Antioxidant

Typical properties (not to be construed as specifications)		Value (SI)	Value (English)	Method
Resin Properties	Melt Index (190°C/2.16kg)	20 g/10min	20 g/10min	ASTM D1238
	Density	0.924 g/cm <sup>3</sup>	0.924 g/cm <sup>3</sup>	ASTM D1505
Product Properties	Tensile strength at yield	15 MPa	2 175 psi	ASTM D638 <sup>1)</sup>
	Tensile strength at break	18 MPa	2 610 psi	ASTM D638 <sup>1)</sup>
	Elongation at break	900 %	900 %	ASTM D638 <sup>1)</sup>
	Flexural modulus	440 MPa	63 800 psi	ASTM D790
	ESCR	> 50 hr	> 50 hr	ASTM D1693 <sup>2)</sup>
	Impact energy at -40°C	20 J/mm	44 ft/lbs	ASTM D5628 <sup>3)</sup>
	Shore D hardness	56	56	ASTM D2240
Vicat softening temperature	97 °C	97 °C	ASTM D1525	

1) Crosshead speed 50 mm/min

2) 100% Igepal CO630

3) Tested on 3mm compression moulded samples

## PRODUCT DATA SHEET



LLDPE LLDPE LLDPE LLDPE LLDPE LLDPE LLDPE LLDPE LLDPE LLDPE

### Injection moulding



### Processing – Injection moulding

HM2420 can be processed over a wide range of temperatures. Typical melt temperatures are 200°C to 240°C. HM2420 can be demoulded at fairly high temperatures due to its higher melting point, which can benefit cycle times.

### Processing – Masterbatch

HM440 processes over a wide range of temperatures. Typical melt temperatures are 180°C to 250°C. HM2420 can be used for various pigment concentrations due to its high flow properties.

### Handling

Workers should be protected from the possibility of skin or eye contact with molten polymer. Safety glasses are suggested as a minimal protection to prevent possible mechanical or thermal injury to the eyes. Fabrication areas should be ventilated to carry away fumes or vapours. Please consult the material safety data sheet (SDS) for more detailed information.

### Storage

As ultraviolet light may cause a change in the material, all resins should be protected from direct sunlight during storage. If stored in cool (<25°C), dry area with low ambient light levels, polyolefin resins are expected to maintain their original material and processing properties for at least 12 months.

### Combustibility

Polyethylene resins will burn when supplied adequate heat and oxygen. They should be handled and stored away from contact with direct flames and/or other ignition sources. In burning, polyethylene resins contribute high heat and may generate a dense black smoke. Fires can be extinguished by conventional means with water and water mist preferred. In enclosed areas, fire fighters should be provided with self contained breathing apparatus.

### Conveying

Conveying equipment should be designed to prevent accumulation of fines and dust particles that are contained in all polyethylene resins. The fines and dust particles can, under certain conditions, pose an explosion hazard. We recommend that the conveying system used:

- be equipped with adequate filters
- is operated and maintained in such a manner to ensure no leaks develop
- that adequate grounding exists at all times

It is further recommended that good housekeeping is practiced throughout the facility.

### Regulatory & Legal Compliance

This material complies with FDA regulation 21 CFR 177.1520 when used unmodified and according to good manufacturing practices for food contact applications. Refer to applicable food contact compliance statement which is available on request. This material is not medically approved and should therefore not be used in any such application.

This publication contains information provided in good faith and is indicative, based on Sasol's current knowledge on the subject. No guarantee or warranty is intended or implied. We reserve the right to make changes as a result of technological progress or development. Any information, including suggestions for use of products, should not preclude experimental testing and verification, to ensure the suitability of a product for each specific application. Users must also abide by local and international laws and obtain all necessary permits when required to do so. Prior to handling a hazardous product, consult it's safety data sheet. In case of questions or queries, please contact Sasol through our customer service channels. All products purchased or supplied by Sasol Chemicals are subject to the terms and conditions set out in the contract, order confirmation and/or bill of lading.

## APPENDIX C: CHARACTERISATION OF NEAT WAXES AND LLDPEs

### GAS AND SIZE EXCLUSION CHROMATOGRAPHY ANALYSIS

#### METHOD

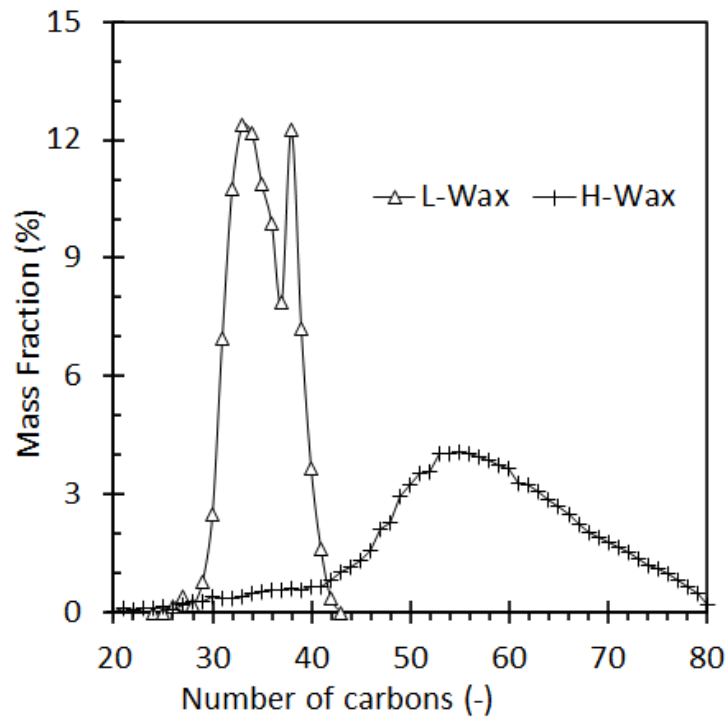
Two waxes were used in this study and their molar mass distributions were determined by Cirrebellle (Randburg, South Africa) using a standard gas chromatography (GC) method. The carbon number distributions were determined using Perkin Elmer Clarus Gas Chromatography 4000. Xylene AR was used as the mobile phase. It was required that the sample vials be heated to above 70 °C to ensure complete solubility of the sample which was injected at this temperature. The waxes comprise of mainly *n*-paraffins with other different types of hydrocarbon molecules including iso-alkanes, alpha-olefins, alcohols and oxygenates present in small amounts. Table C.1 and Figure C.1 shows a breakdown of these components in L-Wax and H-Wax according to GC analysis.

**Table C.1:** Components in L-Wax and H-Wax according to GC analysis

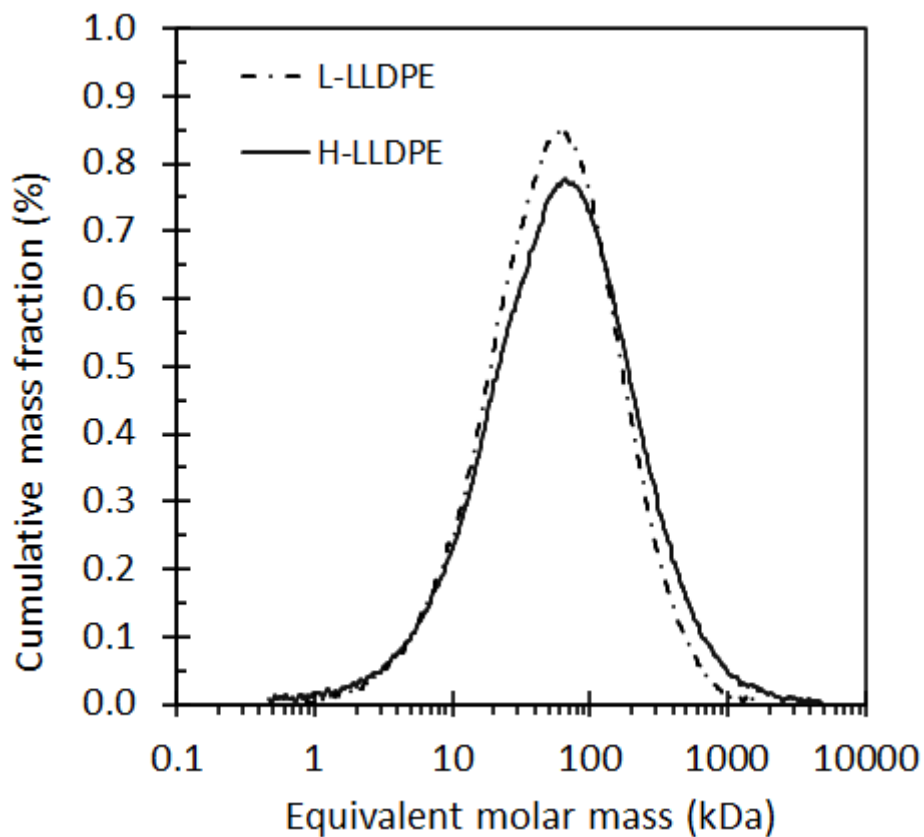
Component (%)	L-Wax	H-Wax
<i>n</i> -paraffins	86.69	98.41
Iso-paraffins	12.66	-
olefins	0.59	-
OH	0.12	-
<b>Total (%)</b>	<b>100</b>	<b>98.41</b>

Two different polymer materials were used, and their molar mass distributions were determined by the Department of Chemistry and Polymer Science, University of Stellenbosch, using size exclusion chromatography (SEC). Results of the molecular mass distribution are shown in figure C.2 and Table C.2

## RESULTS



**Figure C.1:** Molecular mass distribution of L-Wax and H-Wax



**Figure C.2:** Molecular mass distribution of L-LLDPE and H-LLDPE

**Table C.2:** Composition and molecular mass distribution of the F-T waxes and LLDPE are summarized

<b>Sample</b>	<b><math>M</math> (Da)</b>	<b><math>M_n</math> (Da)</b>	<b>PDI</b>
<b>L-Wax</b>	493	490	1.00
<b>H-Wax</b>	786	776	1.01
<b>L-LLDPE</b>	92390	26460	3.49
<b>H-LLDPE</b>	129100	23530	5.49

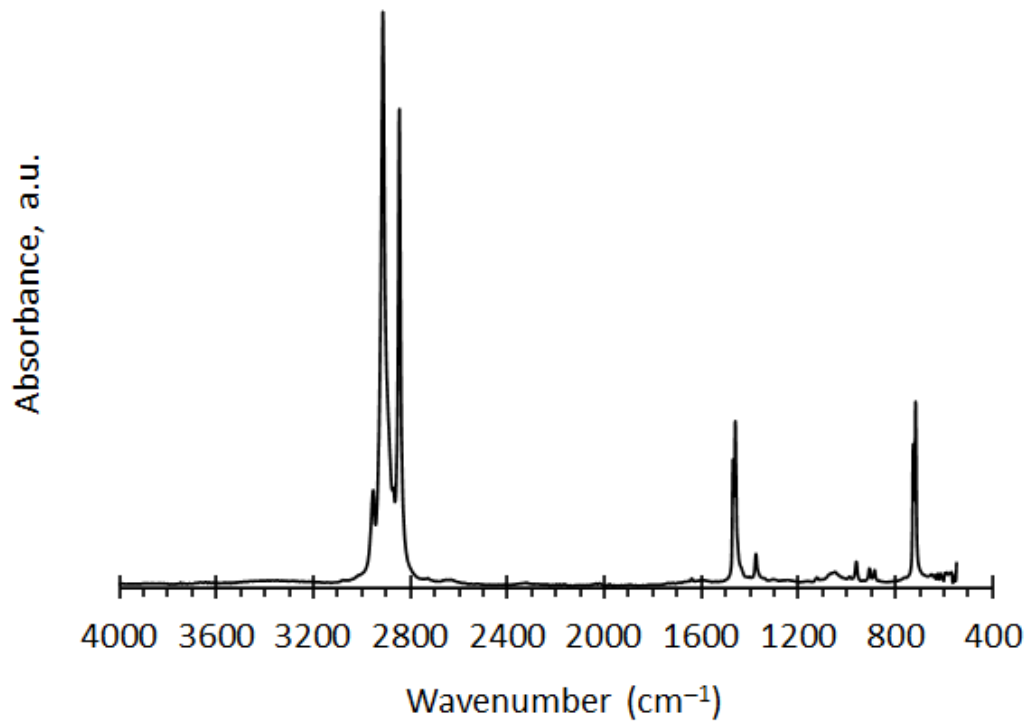
\*PDI - dispersity

## FOURIER TRANSFORM INFRARED SPECTROSCOPY

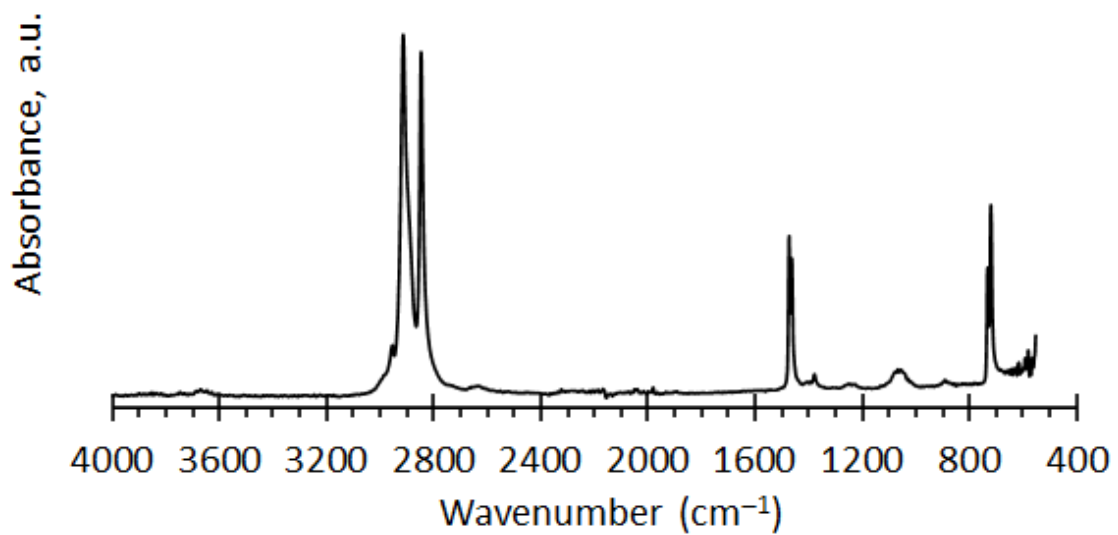
### METHOD

To study the chemical composition and possibility of oxidation of the waxes attenuated total reflectance (ATR) Fourier transform infrared (FT-IR) spectroscopy using a Perkin-Elmer Spectrum 100 spectrometer in the wavelength region of between 550 and 3200  $\text{cm}^{-1}$  was used. The instrument resolution was set on 4  $\text{cm}^{-1}$  with a data interval of 1  $\text{cm}^{-1}$ . The instrument is fitted with a MIR source, optical KBr beamsplitter and windows and a  $\text{LiTaO}_3$  source.

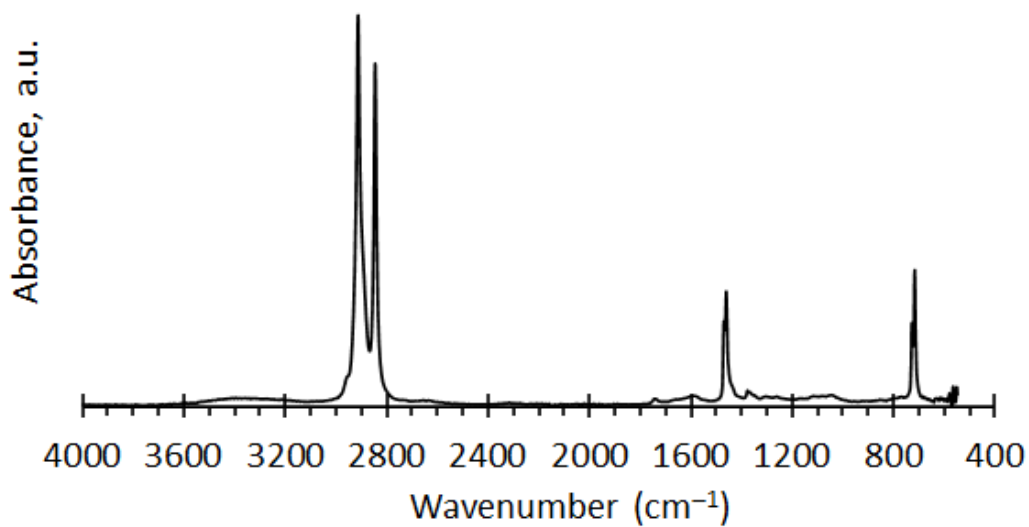
## RESULTS



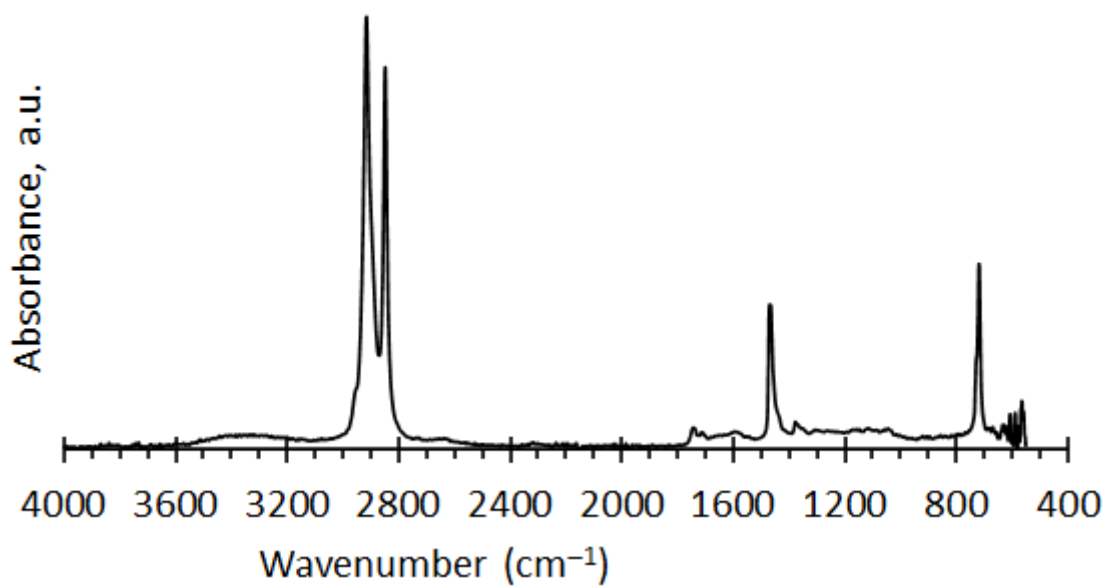
**Figure C.3:** FTIR spectrum of L-Wax



**Figure C.4:** FTIR spectrum of H-Wax



**Figure C.5:** FTIR spectrum of L-LLDPE



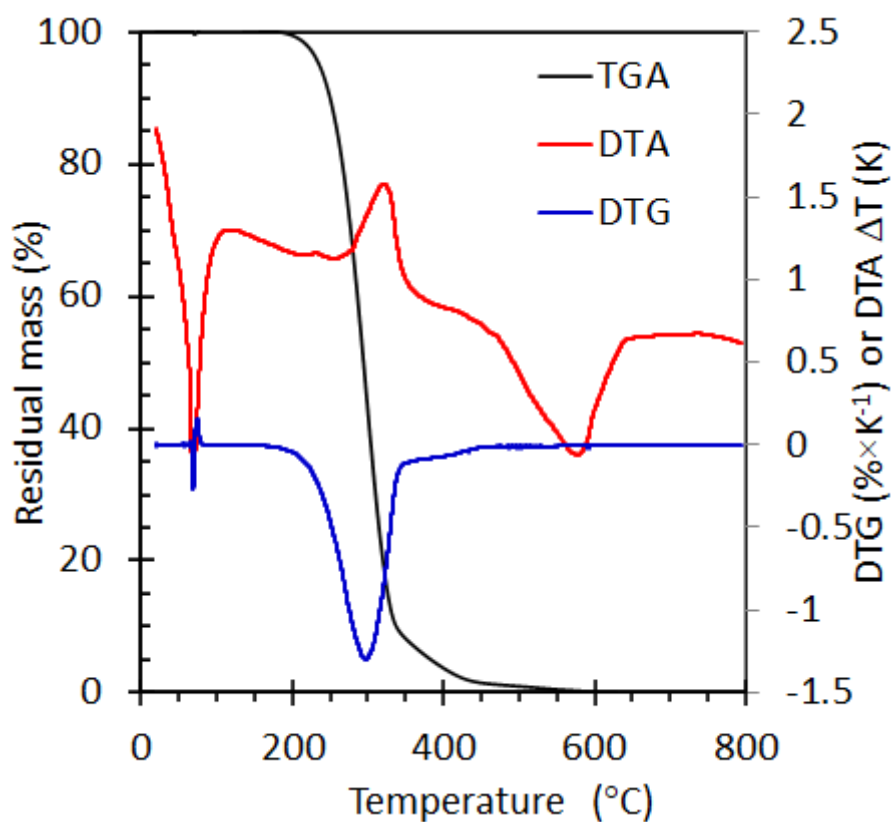
**Figure C.6:** FTIR spectrum of H-LLDPE

## THERMOGRAVIMETRIC ANALYSIS

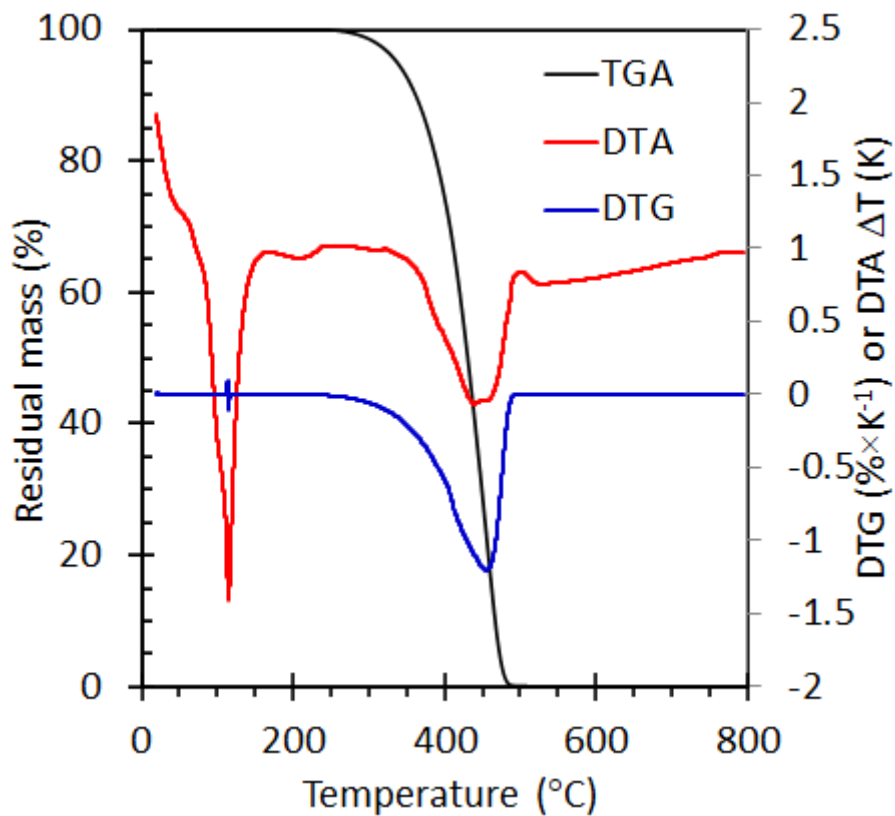
### METHOD

The wax samples were subjected to thermogravimetric analysis in an inert atmosphere of nitrogen. The thermograms were obtained at heating rates  $10\text{ }^{\circ}\text{C min}^{-1}$  up to  $600\text{ }^{\circ}\text{C}$ ,  $50\text{ ml min}^{-1}$   $\text{N}_2$  flow rate, to avoid unwanted oxidation of the sample. An average mass range of 10-20 mg was used in this study.

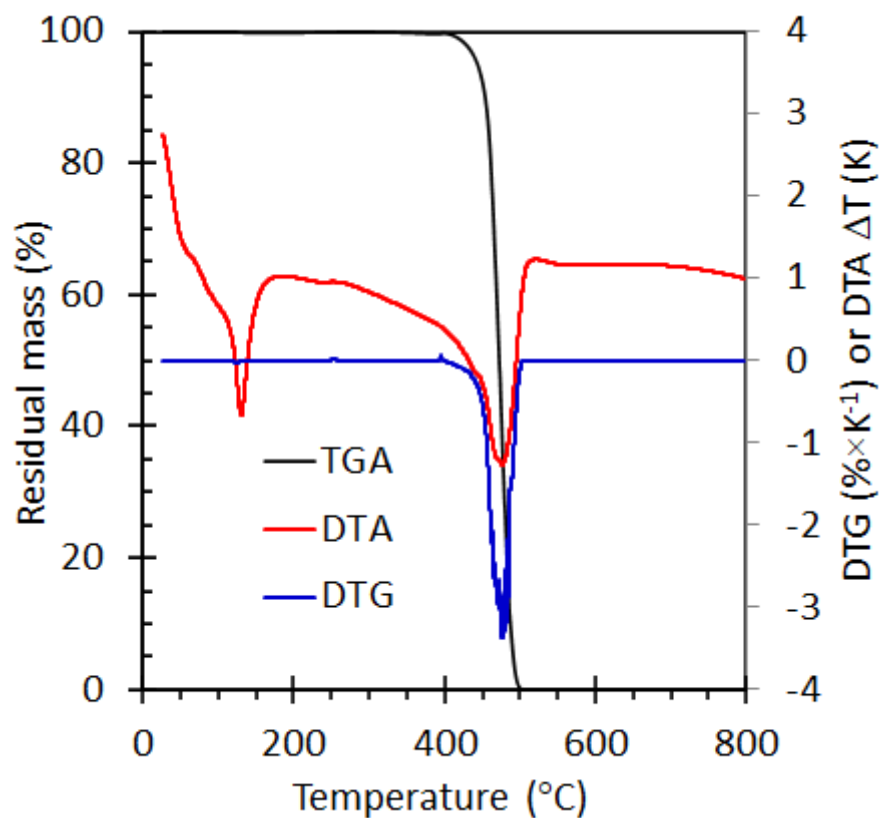
### RESULTS



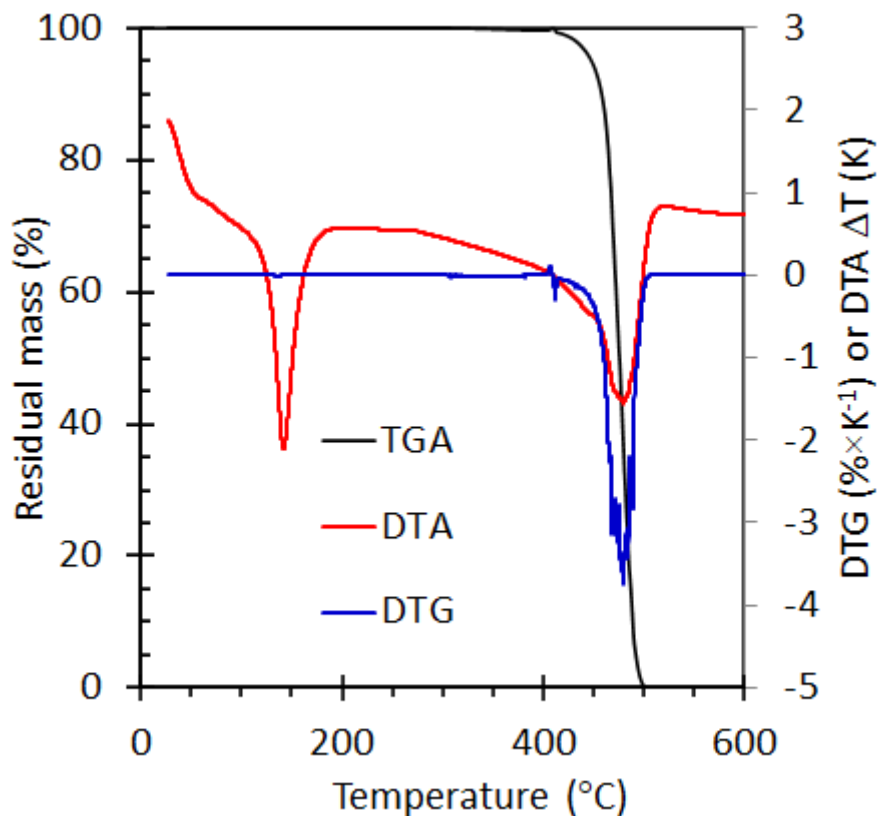
**Figure C.7:** TGA analysis in nitrogen atmosphere of L-Wax



**Figure C.8:** TGA analysis in nitrogen atmosphere of H-Wax



**Figure C.9:** TGA analysis in nitrogen atmosphere of L-LLDPE



**Figure C.10:** TGA analysis in nitrogen atmosphere of H-LLDPE

**Table C.3:** Thermal stability of the neat waxes in terms of 5 %, 50 % and maximum degradation temperatures

Wax sample	T <sub>5%</sub> (°C)	T <sub>50%</sub> (°C)	T <sub>max</sub> (°C)
L-Wax	235.4	294.0	299.2
H-Wax	337.4	430.3	459.1
L-LLDPE	355.2	445.0	470.1
H-LLDPE	320.9	424.3	453.0

## APPENDIX D: FORMULA DERIVATIONS

### Effect of molar mass on zero-shear viscosity of wax/LLDPE melts

Consider blends of compounds of similar chemical structure. The only difference is in the length of the molecules involved. Combinations of hydrocarbon waxes, e.g., Fischer-Tropsch waxes and polyethylene are a good example. At low molar mass, the melt viscosity increases linearly with molar mass. This applies to the wax. Therefore

$$\eta_{o,w} = K_w M_w \quad (1)$$

Above a critical molar mass, the polymer chains become entangled and the zero-shear melt viscosity increases with the 3.4<sup>th</sup> power of weight-average molar mass (Bernard and Noolandi, 1982). This applies to the LLDPE. Therefore:

$$\eta_{o,p} = K_p M^\alpha \quad (2)$$

where the exponent takes on a universal value of  $\alpha = 3.4$ .

The weight average molar mass of a blend is given by:

$$M = w_w M_w + w_p M_p \quad (3)$$

where  $w_w$  and  $w_p$  represent the weight fractions wax and polymer respectively in the binary blend.

The following constraint applies:

$$w_w + w_p = 1 \quad (4)$$

If a blend of two low molar mass compounds is considered, combination of equation (1) with equation (3) leads to the following mixing rule, which should apply if one mixes two waxes:

$$\eta = w_1\eta_1 + w_2\eta_2 \quad (5)$$

If, instead a blend of two polymers are considered, combining equation (2) and (3) leads to the Friedman and Porter (1975) mixing rule:

$$\eta = \left( w_1\eta_1^{1/\alpha} + w_2\eta_2^{1/\alpha} \right)^\alpha \quad (6)$$

Note that this is equivalent to a weighted power-mean of order  $p = 1/\alpha$ . For the wax/polymer blends, the temperature dependence of Equation (6) was “removed” or at least “diminished” by scaling with the viscosity of the neat polymer:

Different, more general approach:

$$M = w_1M_1 + w_2M_2 \quad (7)$$

$$\text{with } \eta_1 = K_1M_1^\beta \quad \text{and} \quad \eta_2 = K_2M_2^\alpha \quad (8)$$

$$M = w_1 \left( \frac{\eta_1}{K_1} \right)^{\frac{1}{\beta}} + w_2 \left( \frac{\eta_2}{K_2} \right)^{\frac{1}{\alpha}} \quad (9)$$

At concentrations approaching pure component 1 the viscosity of the blend should follow a dependence that approaches the dependence defined by component 1:

$$\left( \frac{\eta}{K_2} \right)^{\frac{1}{\alpha}} = w_1 \left( \frac{\eta_1}{K_1} \right)^{\frac{1}{\beta}} + w_2 \left( \frac{\eta_2}{K_2} \right)^{\frac{1}{\alpha}} \quad (10)$$

$$\eta = K_2 \left[ w_1 \left( \frac{\eta_1}{K_1} \right)^{\frac{1}{\beta}} + w_2 \left( \frac{\eta_2}{K_2} \right)^{\frac{1}{\alpha}} \right]^{\alpha} \quad (11)$$

At concentrations approaching pure component 2 the viscosity of the blend should follow a concentration dependence that approaches that of component 2. By analogy to equation (11):

$$\eta = K_1 \left[ w_1 \left( \frac{\eta_1}{K_1} \right)^{\frac{1}{\beta}} + w_2 \left( \frac{\eta_2}{K_2} \right)^{\frac{1}{\alpha}} \right]^{\beta} \quad (12)$$

The two limiting forms can be combined as a weighted power mean in order to define the viscosity trend. A power-mean of order  $p = 1$  corresponds to the arithmetic mean:

$$\eta = w_1 K_1 \left[ w_1 \left( \frac{\eta_1}{K_1} \right)^{\frac{1}{\beta}} + w_2 \left( \frac{\eta_2}{K_2} \right)^{\frac{1}{\alpha}} \right]^{\beta} + w_2 K_2 \left[ w_1 \left( \frac{\eta_1}{K_1} \right)^{\frac{1}{\beta}} + w_2 \left( \frac{\eta_2}{K_2} \right)^{\frac{1}{\alpha}} \right]^{\alpha} \quad (13)$$

Note that the terms in the square brackets are equal to the weight average molar mass of the blends. Simplifying:

$$\eta = w_1 K_1 M^{\beta} + w_2 K_2 M^{\alpha} \quad (14)$$

Note that, if the exponents and the constants  $K_i$  are the same, equation (14) reduces to either equation (5) or equation (6) depending on the value of the exponents.

Proof:

$$\eta = w_1 K_1 M^{\beta} + w_2 K_2 M^{\alpha} = w_1 K M^{\alpha} + w_2 K M^{\alpha} = (w_1 + w_2) K M^{\alpha} = K M^{\alpha}$$

From equation (9):  $M = w_1 \left( \frac{\eta_1}{K} \right)^{\frac{1}{\alpha}} + w_2 \left( \frac{\eta_2}{K} \right)^{\frac{1}{\alpha}}$

$$\eta = KM^\alpha = K \left[ w_1 \left( \frac{\eta_1}{K} \right)^{\frac{1}{\alpha}} + w_2 \left( \frac{\eta_2}{K} \right)^{\frac{1}{\alpha}} \right]^\alpha = \left( w_1 \eta_1^{\frac{1}{\alpha}} + w_2 \eta_2^{\frac{1}{\alpha}} \right)^\alpha$$

Substituting the  $K_i$  values using equation (8) yields the general mixing rule:

$$\eta = w_1 \eta_1 \left( \frac{M}{M_1} \right)^\beta + w_2 \eta_2 \left( \frac{M}{M_2} \right)^\alpha \quad (15)$$

Applied to the present situation, let the wax be represented by component 1 and the polymer by component 2. Then it follows that  $\beta = 1$  and  $\alpha = 3.4$

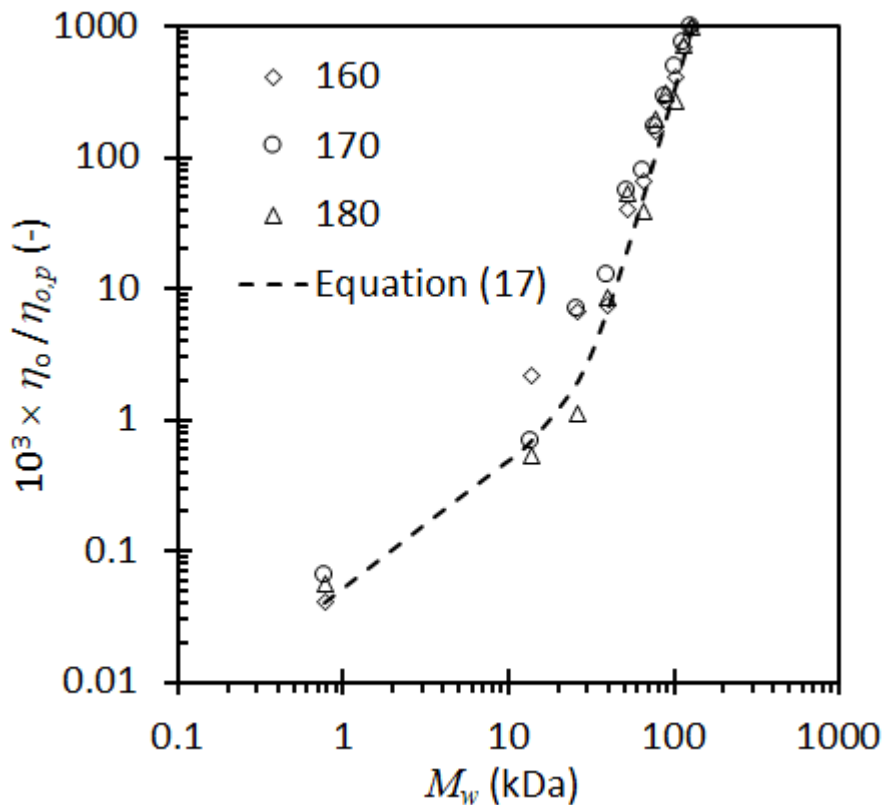
$$\eta = w_w \eta_w \left( \frac{M}{M_w} \right) + w_p \eta_p \left( \frac{M}{M_p} \right)^{3.4} \quad (16)$$

Data was generated at three different temperatures, i.e., 160 °C, 170 °C and 180 °C.

Viscosity is a strong function of temperature. Therefore, in order to suppress the temperature dependence, the experimental data was plotted as  $\eta/\eta_0$ :

$$\frac{\eta}{\eta_p} = w_w \left( \frac{\eta_w M}{\eta_p M_w} \right) + w_p \left( \frac{M}{M_p} \right)^{3.4} \quad (17)$$

The figure shows that the fully predictive equation (17) provided a good fit of the experimental data trends.



**Figure:** Test of the novel zero-shear viscosity mixing rule for F-T wax/LLDPE blends. The data were generated at temperatures of 160 °C, 170 °C and 180 °C.

**Notes:**

**Critical molar mass**

At the critical molar mass ( $M_c$ ), equation (1) and equation (2) predict the same zero-shear viscosity. This condition links the values of the two viscosity constants:

$$K_w = K_p M_c^{\alpha-1} \quad (18)$$

It is sometimes stated that the critical molar mass is a fixed quantity. If that is indeed the case, it implies that the ratio  $K_w/K_p$  is temperature independent.

## Athermal mixtures of chemically dissimilar polymers

It is expected that Equation (15) should also hold for blends of two polymers of different chemistry provided the unlike interactions and like interactions are the same:

$$\eta = \left( \frac{w_1 \eta_1}{M_1^\alpha} + \frac{w_2 \eta_2}{M_2^\alpha} \right) M^\alpha \quad (19)$$

or

$$\eta = \left( w_1 \eta_1 M_2^\alpha + w_2 \eta_2 M_1^\alpha \right) \left( \frac{M}{M_1 M_2} \right)^\alpha \quad (20)$$

## Power mean

$$\eta = w_1 \left[ \left( K_1 M^\beta \right)^p + w_2 \left( K_2 M^\alpha \right)^p \right]^{1/p}$$

$$\eta = \left[ w_1 \left( \eta_1 \left( \frac{M}{M_1} \right)^\beta \right)^p + w_2 \left( \eta_2 \left( \frac{M}{M_2} \right)^\alpha \right)^p \right]^{1/p}$$

## Simple mixing rules proposed for liquid viscosity

Grunberg and Nissan (1949) model:  $\ell n \eta = w_1^2 \ell n \eta_1 + 2w_1 w_2 \ell n \eta_{12} + w_2^2 \ell n \eta_2$

Hind et al. (1960) model:  $\eta = \eta_1 w_1^2 + 2\eta_{12} w_1 w_2 + \eta_2 w_2^2$

**Combining rules** provides a way to express binary parameters in terms of pure component properties. Consider the following possibilities for these models:

Linear combining rule:  $\eta_{12} = (\eta_1 + \eta_2) / 2$

Geometric combining rule:  $\eta_{12} = \sqrt{\eta_1 \eta_2}$

Harmonic combining rule:  $\eta_{12} = 1 / (1/\eta_1 + 1/\eta_2)$

Sotomayor et al. (2014) studied blends of high-density polyethylene with a soft paraffin wax. They assumed the Grunberg and Nissan model with combining rule

$$\ln \eta_{12} = (\ln \eta_1 + \ln \eta_2) / 2$$

Substituting in the Grunberg-Nissan model:

$$\begin{aligned} \ell n \eta &= w_1^2 \ell n \eta_1 + 2w_1 w_2 \ell n \eta_{12} + w_2^2 \ell n \eta_2 \\ &= w_1^2 \ell n \eta_1 + w_1 w_2 (\ln \eta_1 + \ln \eta_2) + w_2^2 \ell n \eta_2 \\ &= w_1^2 \ell n \eta_1 + w_1 w_2 \ln \eta_1 + w_1 w_2 \ln \eta_2 + w_2^2 \ell n \eta_2 \\ &= w_1 (w_1 + w_2) \ln \eta_1 + w_2 (w_1 + w_2) \ln \eta_2 \\ &= w_1 \ln \eta_1 + w_2 \ln \eta_2 \end{aligned}$$

### “Ideal” viscosity

$$\ell n \eta = w_1 \ln \eta_1 + w_2 \ell n \eta_2$$

$$\eta = \eta_1^{w_1} \eta_2^{w_2}$$

$$\Delta \eta = \eta - \eta_1^{w_1} \eta_2^{w_2}$$

where  $\eta$  is the measured viscosity and  $\eta_1$  and  $\eta_2$  are the viscosities of the pure components 1 and 2, respectively.

To get rid of the temperature dependence, a normalized expression can be used:

$$\frac{\Delta \eta}{\eta_1^{w_1} \eta_2^{w_2}} = \frac{\eta}{\eta_1^{w_1} \eta_2^{w_2}} - 1$$

Theoretically, if the Friedman and Porter (1975) model applies, the experimental data should track the following expression

$$\Delta\eta = (w_1\eta_1^{1/\alpha} + w_2\eta_2^{1/\alpha})^\alpha - \eta_1^{w_1}\eta_2^{w_2}$$

$$\frac{\Delta\eta}{\eta_1^{w_1}\eta_2^{w_2}} = \frac{(w_1\eta_1^{1/\alpha} + w_2\eta_2^{1/\alpha})^\alpha}{\eta_1^{w_1}\eta_2^{w_2}} - 1$$

$$\Delta\eta / (\eta_1^{w_1}\eta_2^{w_2})$$

**Problem:** We were unable to measure the pure wax viscosity! So, it had to be estimated assuming the same activation energy holds

## Derivation of the Lederer model

(Lederer, 1931) model:

$$\ln\eta = \frac{x_1}{x_1 + ax_2} \ln\eta_1 + \frac{ax_2}{x_1 + ax_2} \ln\eta_2$$

$$\text{From } w_1 = \frac{M_1 x_1}{M_1 x_1 + M_2 x_2} \quad w_2 = \frac{M_2 x_2}{M_1 x_1 + M_2 x_2} \quad M = M_1 x_1 + M_2 x_2$$

$$\begin{aligned} w_1 &= \frac{M_1 x_1}{M_1 x_1 + M_2 x_2} \\ w_1 M_1 x_1 + w_1 M_2 (1 - x_1) &= M_1 x_1 \\ w_1 M_1 x_1 + w_1 M_2 - x_1 w_1 M_2 &= M_1 x_1 \\ M_1 x_1 + x_1 w_1 M_2 - w_1 M_1 x_1 &= w_1 M_2 \\ (M_1 + w_1 M_2 - w_1 M_1) x_1 &= w_1 M_2 \\ x_1 &= \frac{w_1 M_2}{M_1 + w_1 M_2 - w_1 M_1} \\ x_1 &= \frac{w_1 M_2}{M_1 (w_1 + w_2) + w_1 M_2 - w_1 M_1} \\ x_1 &= \frac{w_1 M_2}{w_1 M_2 + w_2 M_1} \end{aligned}$$

$$\text{Therefore: } x_1 = \frac{w_1 M_2}{w_1 M_2 + w_2 M_1} \quad \text{and} \quad x_2 = \frac{w_2 M_1}{w_1 M_2 + w_2 M_1}$$

$$\frac{x_1}{x_1 + ax_2} = \frac{\frac{w_1 M_2}{w_1 M_2 + w_2 M_1}}{\frac{w_1 M_2}{w_1 M_2 + w_2 M_1} + \frac{aw_2 M_1}{w_1 M_2 + w_2 M_1}} = \frac{w_1 M_2}{w_1 M_2 + aw_2 M_1} = \frac{w_1}{w_1 + a \frac{M_1}{M_2} w_2}$$

$$\begin{aligned} ax_2 &= \frac{w_2 a M_1}{w_1 M_2 + w_2 M_1} \\ \frac{ax_2}{x_1 + ax_2} &= \frac{\frac{w_2 a M_1}{w_1 M_2 + w_2 M_1}}{\frac{w_1 M_2}{w_1 M_2 + w_2 M_1} + \frac{w_2 a M_1}{w_1 M_2 + w_2 M_1}} = \frac{w_2 a M_1}{w_1 M_2 + w_2 a M_1} = \frac{w_2 \frac{a M_1}{M_2}}{w_1 + w_2 \frac{a M_1}{M_2}} \end{aligned}$$

Define  $aM_1/M_2 = b$ , then the Lederer equation can be recast to look the same in mass fractions:

$$\ln \eta = \frac{w_1}{w_1 + bw_2} \ln \eta_1 + \frac{bw_2}{w_1 + bw_2} \ln \eta_2$$