Date: 28 August 2024

Report: 18720/002

Test Report:

- **Compositional Analysis:**
  - Structural Determination: Identification of Polymer Type
  - Elemental Content: Determination of Prodegradant Catalysts

- **Accelerated Ageing Studies:**
  - Polymer Oxidation During Accelerated Ageing:
    - Thermal Stability
    - Thermal Degradation, Following Initial UV Exposure

Test Reference: **18720 Industrias HYC SAS**

Product Tested: **HDPE Clear Film**

Prepared for: **Industrias HYC SAS**

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TEST REPORT

1.0 AIMS

- To determine the polymer composition of the HDPE Clear Film sample by infrared (IR) spectroscopy.
- To evaluate the presence of prodegradant catalysts in the HDPE Clear Film sample by determination of the prodegradant catalyst metal cations by X-ray fluorescence (XRF) spectroscopy.
- To evaluate the stability and degradation behaviour of the HDPE Clear Film sample by means of accelerated laboratory ageing techniques, while monitoring extent of polymer oxidation by infrared (IR) spectroscopy as a function of time.

2.0 SAMPLE DETAILS

Samples Provided by: Industrias HYC SAS
Product Type: HDPE Clear Film
Date Received: 31/07/2024

Table 1: Sample Details

SEPTL Sample ID	Client Reference	Polymer Type	Prodegradant Additive
18720/9138	A040	HDPE	1% d_2w 93224/I

Table 1 is based solely on information provided by the client.

3.0 RESULTS & CONCLUSIONS

3.1 Compositional Analysis

3.1.1 Determination of Polymer Composition

The sample polymer type is determined by infrared (IR) spectroscopy. The infrared spectrum of sample 18720/9138 (Figure 1) demonstrates features corresponding to polyethylene (Table 2).

Weak features corresponding to CH_3 at 1377 cm^{-1} relate to polymer chain terminal groups, their presence indicate a substantial degree of chain branching, i.e., LDPE or LLDPE. Peak splitting of features corresponding to CH_2 vibrations suggest a semi-crystalline character, i.e., HDPE or LLDPE.

There is no evidence of polymer oxidation in sample 18720/9138, as received.

Table 2: Determination of Polymer Type

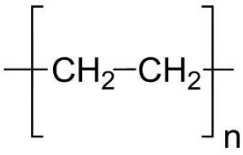
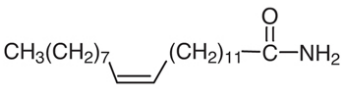
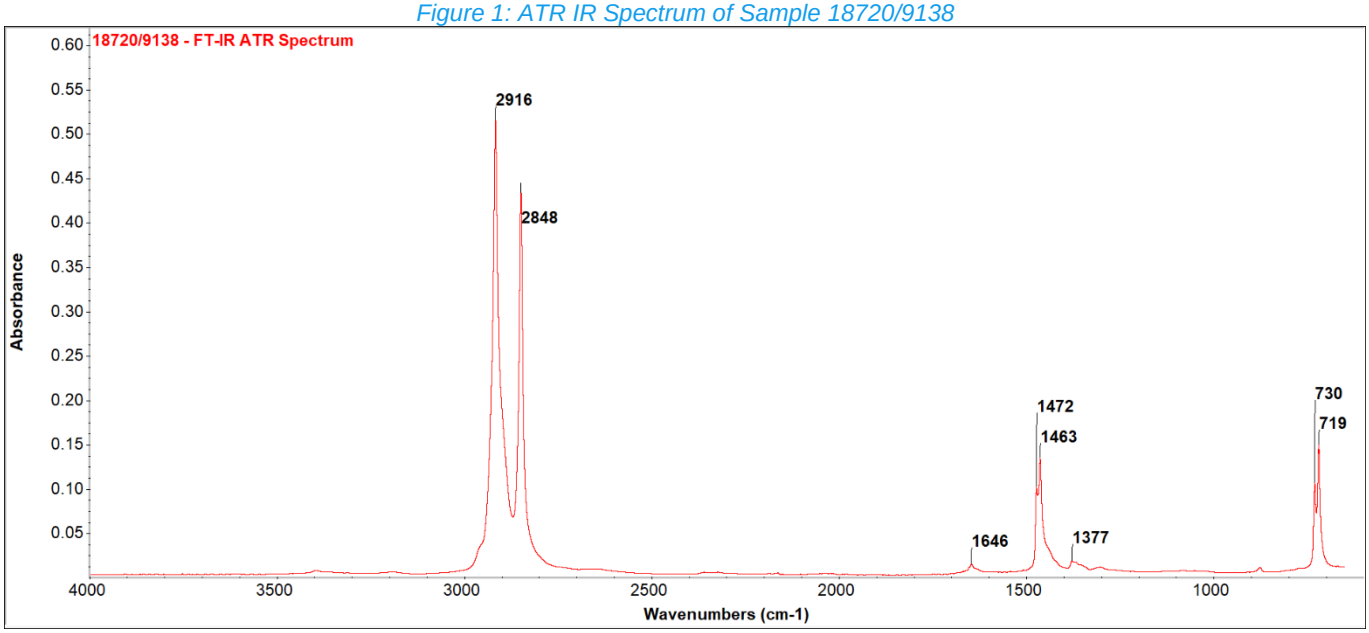
Sample ID	Absorption Bands	Intensity/Shape	Bond Assignment		Polymer/Compound
18720/9138	2916 cm^{-1}	strong, sharp	CH_2 asymmetric C-H stretch		Polyethylene 
	2848 cm^{-1}	strong, sharp	CH_2 symmetric C-H stretch		
	1472 cm^{-1}	medium, sharp; doublet	CH_2 bend	crystalline	
	1463 cm^{-1}			amorphous	
	1377 cm^{-1}	weak, sharp	CH_3 symmetric bend (umbrella mode)		
	730 cm^{-1}	medium, sharp; doublet	CH_2 rock	crystalline	
	719 cm^{-1}			amorphous	
	1646 cm^{-1}	weak, sharp	C=O stretch, amide I		Fatty acid amide, slip agent (e.g.oleamide or erucamide) 

Figure 1: ATR IR Spectrum of Sample 18720/9138



3.1.2 Determination of Prodegradant Catalysts

The presence of prodegradant catalysts in each sample is confirmed by determination of the prodegradant catalyst metal cations by energy-dispersive X-ray fluorescence (XRF) spectroscopy.

The prodegradant catalyst content result, as determined by X-ray fluorescence (XRF) spectroscopy, is given in Table 3.

Table 3: Determination of Prodegradant Catalyst

Sample ID	Spectrum Ref.	Prodegradant Content
18720/9138	212014/2938	Prodegradant Present, Effective Concentration

3.2 Accelerated Ageing

3.2.1 Thermal Stability

The real-time stability of polymer products stored at ambient temperatures and protected from extended exposure to sunlight is evaluated over shorter period of time in the laboratory by monitoring stability and degradation during thermal ageing at elevated temperatures according to ASTM D5510.

Polymer stability and degradation is evaluated by determination of polymer oxidation by infrared spectroscopy in accordance with ISO 10640. The increase in magnitude of features of the infra-red spectra corresponding to the carbonyl products of polymer oxidation, is recorded as carbonyl optical density. The period of accelerated thermal ageing where no significant increase in carbonyl optical density (Table 6) is observed is considered to be representative of the real-time period of product stability in storage conditions.

Sample 18720/9138 demonstrated a significant increase in carbonyl optical density measurement at the conclusion of the test (Table 4/Figure 2). This result is consistent with the sample having undergone significant degradation.

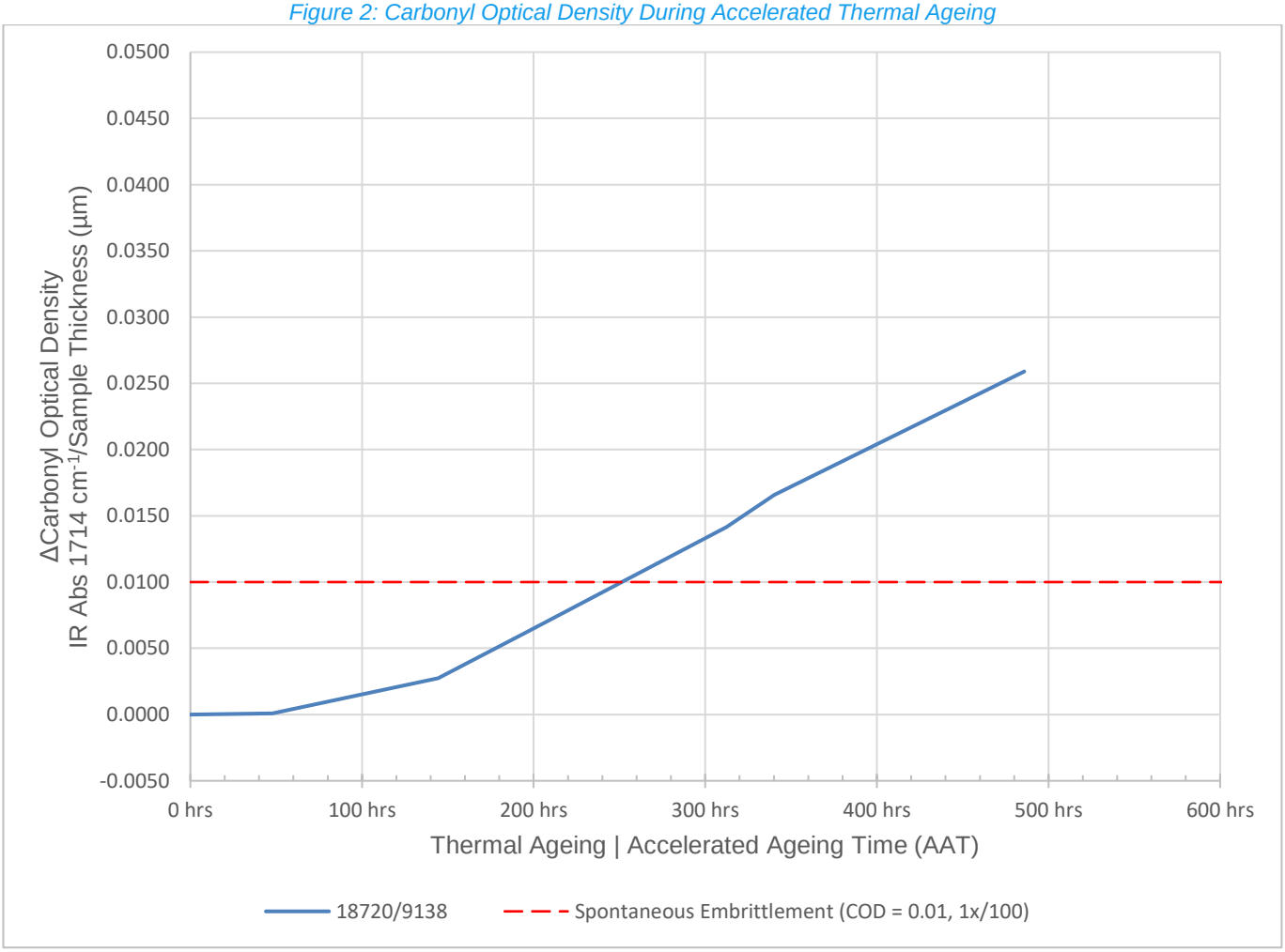
The observation of degradation of the sample shows that the product is not stable to thermal ageing. This indicates that the product is vulnerable to premature degradation.

The use of product formulation designed provide a greater extent of stabilisation will be likely to extend the shelf-life of this product.

Table 4: Carbonyl Optical Density During Accelerated Thermal Ageing

Accelerated Ageing Time (AAT)	ΔCarbonyl Optical Density (IR Abs 1714 cm^{-1}/Thickness)
	18720/9138
0 hrs	0.0000
48 hrs	0.0001
144 hrs	0.0027
194 hrs	0.0061
312 hrs	0.0142
340 hrs	0.0166
486 hrs	0.0259

Figure 2: Carbonyl Optical Density During Accelerated Thermal Ageing



3.2.2 Thermal Degradation, Following Initial UV Exposure

Polymer degradation in dark conditions, following initial exposure to sunlight is evaluated in a shorter period of time in the laboratory by monitoring degradation during accelerated fluorescent UV ageing in accordance with ASTM D5208 followed by thermal ageing at elevated temperatures according to ASTM D5510.

Polymer degradation is evaluated by determination of polymer oxidation by infrared spectroscopy in accordance with ISO 10640. The increase in magnitude of features of the infra-red spectra corresponding to the carbonyl products of polymer oxidation, is recorded as carbonyl optical density. An increase in carbonyl optical density of 0.0100 corresponds to a >95% reduction in mechanical properties and is therefore considered indicative of advanced degradation as such to bring about spontaneous embrittlement (Table 6). The rate of degradation is evaluated and compared by monitoring carbonyl optical density as a function of ageing time.

3.2.2.1 48 hours Initial UV Exposure

The sample was initially exposed to constant fluorescent UV ageing for a period of 48 hours. The sample was then exposed to accelerated thermal ageing in dark conditions.

Sample 18720/9138 demonstrated a significant increase in carbonyl optical density (Table 5/Figure 3). This result is consistent with this sample having undergone significant degradation.

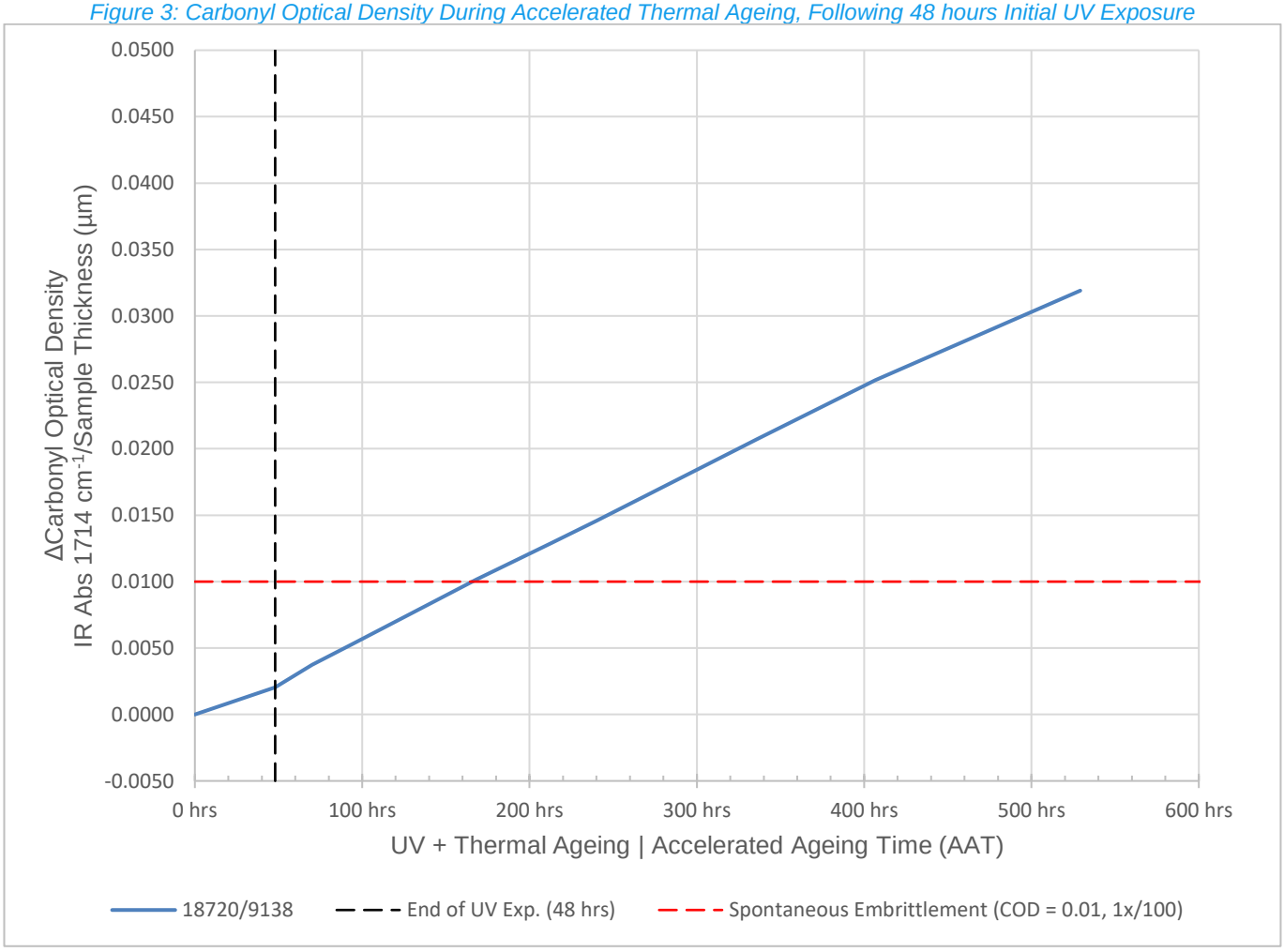
A carbonyl optical density value of ≥0.0100 is consistent with oxidation and molecular weight reduction of the polymer film sufficient to bring about a substantial reduction in mechanical properties (Table 6), this together with an observation of spontaneous embrittlement of the sample is sufficient to confirm an absolute elongation at break of 5% or less, according to ASTM D3826.

The observation of degradation in the sample which contains the prodegradant additive is consistent with the prodegradant catalyst promoting degradation of the product in dark conditions, following initial exposure to sunlight in the environment as litter.

Table 5: Carbonyl Optical Density During Accelerated Thermal Ageing, Following 48 hours Initial UV Exposure

Accelerated Ageing Time (AAT)	Exposure	ΔCarbonyl Optical Density (IR Abs 1714 cm^{-1}/Thickness)
		18720/9138
0 hrs	UV	0.0000
48 hrs		0.0020
70 hrs	Thermal	0.0037
94 hrs		0.0053
168 hrs		0.0102
213 hrs		0.0129
240 hrs		0.0146
336 hrs		0.0207
407 hrs		0.0252
529 hrs		0.0319

Figure 3: Carbonyl Optical Density During Accelerated Thermal Ageing, Following 48 hours Initial UV Exposure



4.0 TEST METHODOLOGY

4.1 FT-IR Spectroscopy

4.1.1 Structural Determination: Identification of Polymer Type

For characterisation of polymer composition, the infrared (IR) spectra are recorded by attenuated total reflection (ATR), in accordance with ISO 10640 using a Thermo Scientific Nicolet iS10 Fourier transform infrared (FT-IR) spectrometer fitted with a smart iTR accessory and diamond ATR crystal. Spectra are collected across the range of 650 to 4,000 cm^{-1}, ≥16 scans, with a resolution of 4 cm^{-1}.

4.1.2 Polymer Oxidation

For determination of polymer oxidation, the infrared (IR) spectra are recorded by transmission, in accordance with ISO 10640 using a Thermo Scientific Nicolet iS10 Fourier transform infrared (FT-IR) Spectrometer fitted with a transmission accessory. Spectra are collected across the range 650 to 4,000 cm^{-1}, ≥16 scans, with a resolution of 4 cm^{-1}.

4.1.2.1 Carbonyl Optical Density Calculation

The extent of oxidation is reported as the carbonyl optical density, a function of the net increase in infrared carbonyl (C=O) absorbance at 1714 cm^{-1} during ageing, per unit of the path length (sample thickness in µm):

Equation 1: $$Carbonyl\ Optical\ Density = \frac{IR\ Abs_{1714\ cm^{-1}}}{Thickness\ (\mu m)}$$

4.1.2.1.1 Extent of Oxidation, Interpretation of Carbonyl Optical Density

The carbonyl optical density value may be interpreted to indicate the approximate extent of degradation of polyolefin films, according to Table 6.

Table 6: Carbonyl Optical Density, Indicated Extent of Degradation

Carbonyl Optical Density	Extent of Degradation
0.000	No significant degradation
0.001	~50% reduction in mechanical properties (EaB)
0.010	Spontaneous Embrittlement, ~>95% reduction in mechanical properties (EaB)
≥0.030	Significant Biodegradability

4.2 XRF Spectroscopy

The XRF spectrum of each unaged sample is recorded using a Bruker S2 Puma Series 2 benchtop spectrometer in air over 120 s live time, using an Ag X-ray anode and graphene window detector, with a 40.00 kV voltage, automatic current settings (300 kcps), and a 500.0 µm aluminium filter. Film samples were prepared in 38 mm diameter HDPE XRF sample cups and the total thickness made up to ~200 µm with 36 mm discs cut from the bulk material using a James Heal 230/10 sample cutter.

4.2.1 Determination of Prodegradant Catalyst

The concentration of prodegradant catalyst metal cations is quantified by correlation with a calibration of validated reference samples.

4.3 Accelerated Ageing Exposure

4.3.1 Sample Preparation/Holders

35 x 90 mm film samples were cut using a scalpel and secured in a sample holder with four exposure windows.

4.3.2 Thickness Determination

The thickness of the sample material is determined before ageing using a digital electronic micrometer, in not less than four random locations across the test sample and the average value recorded.

4.3.3 Accelerated Thermal Ageing

Thermal ageing of the samples was carried out in a Memmert UFE 600 fan assisted oven at a temperature of 70ºC in accordance with ASTM D5510 Procedure B: Forced Ventilation Oven.

4.3.3.1 Thermal Stability Real Time Exposure Prediction

The real-time period (RT) at ambient temperature (T_{RT}) represented by accelerated ageing time (AAT) at elevated accelerated ageing temperature (T_{AA}) is predicted in accordance with ASTM F1980 using the relationship outlined in Equation 2.

The calculation is performed using an anticipated average storage exposure temperature (T_{RT}) of 30°C and a conservative ageing factor (Q_{10}) of 2.

Equation 2: $$AAT = \frac{RT}{Q_{10}^{[(T_{AA}-T_{RT})/10]}}$$

4.3.4 Accelerated Fluorescent UV Ageing

Samples were exposed to ultraviolet radiation in accordance with ASTM D5208 in a Q Panel QUV/se test apparatus fitted with UVA 340 lamps, set to a black panel temperature of 50ºC and irradiance of 0.78 W/m^2/nm @ 340 nm.

5.0 REPORT HISTORY

Date	Report Ref.	Author	Comments
Previous Version			
08/08/2024	18720/001	YB	Updated accelerated ageing data
Current Version – this report supersedes all previous versions			
28/08/2024	18720/002	YB	Added accelerated ageing data

6.0 REPORT AUTHORISATION

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Date: 2024.08.28 13:04:09 +01'00'