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Evaluation of thermal and oxidative stability of three generations of phenolic based novel dendritic fuel and lubricant additives

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Abstract: Antioxidants, particularly those designed for use in hydrocarbon media, suffer from a variety of limitations including high volatility and poor solubility. Using 2,2-bis(hydroxymethyl)propionic acid as the branching unit, a series of novel dendrons featuring 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic ester chain ends have been synthesised to provide improved solubility of such hindered phenolic antioxidants. The thermal stability, assessed by thermogravimetric analysis, revealed that all the functionalised dendrons have enhanced thermal stability when compared to commercial antioxidants (BHT, Irganox L135 and Irganox L57). Antioxidant ability was evaluated using pressurised differential scanning calorimetry and when blended with a lubricant base oil, at 0.5% w/w, an increase in antioxidant performance was observed when compared to the commercial antioxidants.

Keywords: Antioxidants, Dendritic, Oxidation stability, Thermal stability, Oxidation induction time

1. Introduction

With a constant effort to reduce worldwide automotive emissions and meet the ever-tightening environmental legislation controlling Original Equipment Manufacturers (OEMs),

innovative hydrocarbon-based fluid formulations are required to assure vehicle performance and efficiency at the design parameters. The requirement for enhanced fuel efficiency and lower tailpipe CO_2 emissions is a growing demand, which can be achieved through the use of fuel and lubricant additives designed to protect the engine from deterioration. The oxidative degradation of organic materials has been studied for many years and materials derived from petroleum, such as fuels and lubricants, are particularly susceptible as a result of increasingly harsher conditions within a combustion engine. [4-7] High temperatures and pressures in the presence of air and metal surfaces or contaminants contribute to the acceleration of oxidative degradation. [8-9] The oxidation process of liquid hydrocarbons was first proposed by Bolland and Gee in 1946 who described a free radical pathway. [10,11] Since then, the mechanism of oxidation has been investigated extensively and these studies highlighted a complex process where by-products are formed such as acids, alcohols, aldehydes, ketones and higher molecular weight hydrocarbons. [8,9,12-16] Collectively, these by-products cause discolouration, carbonaceous deposition, increased oil viscosity and eventually can lead to physical failure of the combustion engine. The rate of this detrimental process can be decreased if alkyl peroxy radicals, produced in the oxidative process, are scavenged efficiently. Additives such as antioxidants are introduced into hydrocarbon materials to extend their lifetime. A class of compounds described as hindered phenolics have been studied comprehensively for their radical scavenging ability in petroleum based-products. [17-22] It has been found that phenolic antioxidants act by interrupting the reported [10] radical pathway by providing a more labile hydrogen atom when compared to the hydrocarbon species. This scavenging mechanism is highlighted in Figure 1 for the antioxidant butylated hydroxytoluene (BHT) and shows that phenolic antioxidants can directly remove a number of radicals from the oxidation chain reaction. This is achieved by both liberation of a hydrogen radical and through radical coupling processes, consequently inhibiting the oxidation pathway [9].

Numerous examples of both synthetic and naturally occurring sterically hindered phenols have been reported to date (see Figure 2) and structure-activity relationships of these materials have been determined. [23-28] Antioxidants are, however, eventually consumed either through chemical loss, from their antioxidant action, or physical loss. [16,29,30] Physical loss is influenced by factors such as volatilisation and precipitation out of the hydrocarbon matrix and such decreases are often compensated by the addition of excess antioxidant at the outset. [16,29-31] This simplistic solution does, however, have its own disadvantages since many of the antioxidants used often exhibit limited solubility in hydrocarbons and are also relatively expensive. [30,32] In an attempt to overcome the solubility and efficacy issues that face these hydrocarbon additives, a series of phenolic-based branched oligomers with an increasing number of antioxidant end group units were prepared in this study. A branched alkyl chain was utilised to aid the solubility of these phenolic-based branched oligomers in hydrocarbon media such as base oils. The antioxidant potencies were then evaluated using a series of thermal and oxidative tests including thermogravimetric analysis (TGA) and pressurised differential scanning calorimetry (PDSC).

2. Experimental

2.1. General procedure for purification and characterisation

Reagents and solvents were purchased from Sigma Aldrich and used without further purification except for 3-(3,5-di-*tert*-butyl-4-hydroxy-phenyl)-propionic acid which was purchased from Alfa Aesar. All of the solvents used were dried and freshly distilled prior to use. Tetrahydrofuran (THF) was distilled under a nitrogen atmosphere from sodium and benzophenone. Dichloromethane was distilled under a nitrogen atmosphere from calcium hydride. Thin layer chromatography (TLC) was performed on aluminium sheets coated with Merck silica gel 60 F_{24}. Spots were visualised under ultra-violet light (254 nm) with potassium

permanganate as the visualising agent. Column chromatography was performed using Merck silica gel 60 (40-63 µm particle size) and a mobile phase as specified. Melting points were recorded using a Stuart MP10 melting point apparatus. ^{1}H NMR and ^{13}C NMR spectra were recorded using either $CDCl_3$ or DMSO-d_6 as solvent on either a Bruker Nanobay 400 or Bruker DPX 400 operating at 400 MHz for ^{1}H NMR or at 100 MHz for ^{13}C NMR. Infrared (IR) spectroscopic analysis was carried out using a Perkin Elmer 100 FT-IR instrument with a diamond ATR sampling attachment with samples either as solids or oils. Mass spectrometry analysis was carried out on a Thermo-Fisher Scientific Orbitrap XL LC-MS. Samples were prepared as methanol solutions (1 mg/mL) and were ionised using electrospray ionisation (ESI) and the parent mass ions were quoted.

2.2. Synthesis

*2.2.1. 2,2,5-trimethyl-1,3-dioxane-5-carboxylic acid (**2**)*

2,2-Bis(hydroxymethyl)propanoic acid (bis(MPA)) **1** (10.00 g, 74.6 mmol), 2,2-dimethoxypropane (13.8 mL, 111.8 mmol) and *p*-toluene sulfonic acid (*p*-TsOH) (0.71 g, 3.7 mmol) were dissolved in acetone (50 mL). The reaction was stirred at room temperature for 2 hours. The catalyst was neutralised with 1.0 mL of NH_3/EtOH (50:50). The solvent was removed *in vacuo* and the resulting residue was dissolved in dichloromethane (200 mL) and extracted with two portions of water (40 mL). The organic phase was dried over magnesium sulfate ($MgSO_4$), filtered and then evaporated to yield **2** as a white waxy solid (10.32 g, 80%); ^{1}H NMR (400 MHz/$CDCl_3$)/ppm, δ = 1.21 (s, 3H, -CH_3), 1.42 (s, 3H, -CH_3), 1.45 (s, 3H, -CH_3), 3.68 (d, 2H, *J* = 12.0 Hz, -CH_2O, *equatorial*), 4.20 (d, 2H, *J* = 12.0 Hz, -CH_2O, *axial*); ^{13}C NMR (100 MHz/$CDCl_3$)/ppm, δ = 18.4, 21.8, 25.4, 41.7, 65.9, 98.4, 180.0; Found $[M+H]^+$ ($C_8H_{14}O_4$) m/z = 175.0964 (Calc. 175.0965); IR (ATR) *v*/cm^{-1}: 2984, 1719, 1072, 825, 717.

*2.2.2. Preparation of the first generation acetonide (**3**) and general esterification procedure*

2-Ethylhexan-1-ol (7.30 mL, 47.0 mmol), 2,2,5-trimethyl-1,3-dioxane-5-carboxylic acid (**2**) (9.00 g, 51.7 mmol) and DPTS (60%) were dissolved in dry dichloromethane (40 mL). The solution was stirred at room temperature for 30 minutes. To the solution, *N,N'*-dicyclohexylcarbodiimide (DCC) (12.60 g, 61.1 mmol) dissolved in dry dichloromethane (40 mL) was added over 15 minutes. The reaction was left overnight at room temperature under a nitrogen atmosphere. The reaction mixture was filtered to remove the white *N,N'*-dicyclohexylurea (DCU) precipitate and the filtrate was concentrated. The crude product was dissolved in dichloromethane and washed sequentially with 0.5 M HCl and saturated $NaHCO_3$. The organic phase was dried over $MgSO_4$, filtered and the solvent was removed *in vacuo* to yield a pale-yellow oil. Hexane was added to the crude product and the resulting white precipitate was filtered off. The solvent was once again removed *in vacuo* and the resulting oil was purified by flash column chromatography on silica eluting with hexane/ethyl acetate (95:5) (R_f = 0.23) to afford **3** as a thin colourless oil (9.50 g, 71%); ^{1}H NMR (400 MHz/$CDCl_3$)/ppm, δ = 0.90 (s, 3H, -CH_3), 1.21 (s, 3H, -CH_3), 1.30 (m, 6H, -CH_2), 1.39 (s, 3H, -CH_3), 1.43 (s, 3H, -CH_3), 1.61 (m, 1H, -CH) 3.63 (d, 2H, *J* = 12.0 Hz, -CH_2O), 4.07 (m, 2H, -CH_2), 4.17 (d, 2H, *J* = 12.0 Hz, -CH_2O); ^{13}C NMR (100 MHz/$CDCl_3$)/ppm, δ = 11.0, 14.0, 18.7, 23.0, 23.8, 24.2, 28.9, 30.4, 38.8, 41.9, 66.0, 67.0, 98.0, 174.3; Found $[M+H]^+$ ($C_{16}H_{30}O_4$) m/z = 287.2222 (Calc. 287.2223); IR (ATR) *v*/cm^{-1}: 2934, 1735, 1158, 1080.

*2.2.3. Preparation of the first generation hydroxyl linker (**4**) and general procedure for removal of acetonide protecting group*

First generation acetonide **3** (2.5 g, 8.73 mmol) was dissolved in methanol (30 mL) and DOWEX 5W-X8 resin (*ca*. 2 g) was added. The solution was stirred at 50 °C and monitored by TLC analysis, using hexane/ethyl acetate (80:20) as the eluent, until the deprotection was

complete. The resin was filtered off and the filtrate was concentrated *in vacuo* to yield **4** as a colourless viscous oil (2.02 g, 94%); ^{1}H NMR (400 MHz/$CDCl_3$)/ppm, δ = 0.90 (m, 6H, -CH_3), 1.08 (s, 3H, -CH_3), 1.36 (m, 8H, -CH_2), 1.60 (m, 1H, -CH) 3.08 (t, 2H, *J* = 16.0 Hz, -OH), 3.72 (m, 2H, -CH_2O), 3.88 (m, 2H, -CH_2O), 4.09 (m, 2H, -CH_2); ^{13}C NMR (100 MHz/$CDCl_3$)/ppm, δ =11.0, 14.0, 17.2, 22.9, 23.8, 28.9, 38.7, 49.2, 67.3, 68.0, 176.1; Found $[M+H]^+$ ($C_{13}H_{27}O_4$) m/z = 247.1909 (Calc. 247.1910); IR (ATR) *v*/cm^{-1}: 3458, 2694, 1722, 1042.

*2.2.4. Preparation of the second generation acetonide (**5**)*

2,2,5-Trimethyl-1,3-dioxane-5-carboxylic acid **2** (4.88 g, 28.01 mmol), first generation hydroxyl linker **4** (3.00 g, 12.18 mmol), DPTS (60%) and DCC (5.78 g, 28.01 mmol) were allowed to react following the general esterification procedure. The crude product was purified by flash column chromatography on silica eluting with hexane/ethyl acetate (90:10) (R_f = 0.05) increasing polarity to (80:20) to afford **5** as a colourless oil (4.60 g, 70%); ^{1}H NMR (400 MHz/$CDCl_3$)/ppm, δ = 0.89 (m, 6H, CH_3), 1.16 (s, 6H, CH_3), 1.29-1.42 (m, 23H, CH_2 and CH_3), 1.59 (m, 1H, CH), 3.63 (d, 4H, *J* = 12 Hz, CH_2), 4.05 (m, 2H, CH_2), 4.16 (d, 4H, *J* = 12 Hz, CH_2), 4.33 (s, 4H, CH_2); ^{13}C NMR (100 MHz/$CDCl_3$)/ppm, δ = 10.9, 14.0, 17.8, 18.5, 22.4, 23.7, 24.8, 28.9, 30.3, 38.7, 42.0, 46.8, 65.3, 65.9, 67.6, 98.1, 172.6, 173.5; Found $[M+Na]^+$ ($C_{29}H_{50}O_{10}Na$) m/z = 581.3295 (Calc. 581.3296); IR (ATR) *v*/cm^{-1}: 2966, 1734, 1079, 831.

*2.2.5. Preparation of the second generation hydroxyl linker (**6**)*

The second generation acetonide **5** (3.9 g, 7.0 mmol) was dissolved in methanol (40 mL). Using the general procedure for removal of the acetonide protective group described above, **6** was obtained as a waxy solid (2.32 g, 70%); Mp (38-41 °C); ^{1}H NMR (400 MHz/$CDCl_3$)/ppm, δ = 0.90 (m, 6H, -CH_3), 1.05 (s, 6H, -CH_3), 1.31 (m, 11H, -CH_3, -CH_2), 1.59 (m, 1H, -CH), 3.22 (m, 4H, -OH), 3.71 (m, 4H, -CH_2), 3.83 (m, 4H, -CH_2), 4.07 (m, 2H, -CH_2), 4.27 (d, 2H, *J* = 12 Hz, -CH_2), 4.45 (d, 2H, *J* = 12 Hz, -CH_2); ^{13}C NMR (100 MHz/$CDCl_3$)/ppm, δ =

10.9,14.0, 17.1, 18.2, 22.9, 23.7, 28.9, 30.4, 38.7, 46.5, 49.7, 64.8, 67.8, 68.1, 173.1, 175.2; Found $[M+H]^+$ ($C_{23}H_{43}O_{10}$) m/z = 479.2836 (Calc. 479.2851); IR (ATR) *v*/cm^{-1}: 3284, 2940, 1733, 1240, 1115, 1044.

*2.2.6. Preparation of the third generation acetonide (**7**)*

2,2,5-Trimethyl-1,3-dioxane-5-carboxylic acid **2** (9.43 g, 54.16 mmol), second generation hydroxyl linker **6** (4.32 g, 9.03 mmol), DPTS (60%) and DCC (11.18 g, 54.16 mmol) were allowed to react according to the general esterification procedure. The crude product was purified by flash column chromatography on silica eluting with hexane/ethyl acetate (70:30) increasing polarity to (50:50) (R_f = 0.28) to afford **7** as a white waxy solid (5.95 g, 60%); ^{1}H NMR (400 MHz/$CDCl_3$)/ppm, δ = 0.89 (t, 6H, *J* = 12Hz, -CH_3), 1.15 (s, 12H, -CH_3), 1.27 (m, 16H, -CH_3), 1.35 (s, 13H, -CH_3 and -CH_2), 1.41 (s, 12H, -CH_3), 1.60 (m, 1H, -CH), 3.62 (d, 8H, *J* = 12 Hz, -CH_2), 4.03 (m, 2H, -CH_2), 4.15 (d, 8H, *J* = 12 Hz, -CH_2), 4.26 (m, 4H, -CH_3), 4.31 (m, 8H, -CH_3); ^{13}C NMR (100 MHz/$CDCl_3$)/ppm, δ =10.9, 14.1, 17.7, 18.5, 22.2, 22.9, 23.7, 25.1, 28.9, 30.3, 38.7, 42.0, 46.7, 46.8, 64.9, 66.0, 67.9, 98.1, 171.9, 172.1, 173.5; Found $[M+Na]^+$ ($C_{55}H_{90}O_{22}Na$) m/z = 1125.5800 (Calc. 1125.5824); IR (ATR) *v*/cm^{-1}:2937, 1723, 1079, 830.

*2.2.7. Preparation of the third generation hydroxyl linker (**8**)*

The third generation acetonide **7** (3.83 g, 3.5 mmol) was dissolved in methanol (40 mL). Using the general procedure for removal of the acetonide protective group described above, **8** was obtained as a white waxy solid (3.03 g, 79%); ^{1}H NMR (400 MHz/DMSO-d_6)/ppm, δ = 0.85 (m, 6H, -CH_3), 1.01 (s, 12H, -CH_3), 1.17 (s, 6H, -CH_3, -CH_2), 1.20 (s, 3H, -CH_3), 1.26 (m, 8H, -CH_2), 1.56 (m, 1H, -CH), 3.46 (m, 16H, -CH_2), 3.99 (m, 2H, -CH_2), 4.11 (m, 12H, -CH_2), 4.65 (t, 8H, *J* = 12Hz, -OH); ^{13}C NMR (100 MHz/DMSO-d_6)/ppm, δ = 10.7, 13.8, 16.7, 16.9, 17.1, 22.3, 23.2, 28.2, 29.7, 38.0, 46.2, 46.3, 50.2, 63.6, 64.5, 65.8, 171.8, 172.0, 174.0; Found

$[M+H]^+$ ($C_{43}H_{75}O_{22}$) m/z = 943.4751 (Calc. 943.4745); IR (ATR) *v*/cm^{-1}: 3278, 2934, 1727, 1119, 1043.

*2.2.8. Preparation of first generation diphenol (**10**)*

3-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)propanoic acid **9** (3.40 g, 12.17 mmol), first generation hydroxyl linker **4** (1.00 g, 4.059 mmol), DPTS (60%) and DCC (2.51 g, 12.17 mmol) were allowed to react according to the general esterification procedure. The crude product was purified by flash column chromatography on silica eluting with hexane/ethyl acetate (90:10) (R_f = 0.38) to afford **10** as a viscous colourless oil (2.34 g, 75%); ^{1}H NMR (400 MHz/$CDCl_3$)/ppm, δ = 0.88 (m, 6H, -CH_3), 1.16 (s, 3H, -CH_3), 1.33 (m, 8H, -CH_2), 1.43 (s, 36H, -CH_3), 1.61 (m, 1H, -CH), 2.60 (t, 4H, *J* = 16 Hz, -CH_2), 2.85 (t, 4H, *J* = 16.0 Hz, -CH_2), 4.04 (m, 2H, -CH_2), 4.23 (s, 4H, -CH_2), 5.08 (s, 2H, -OH), 6.98 (s, 4H, -ArCH); ^{13}C NMR (100 MHz/$CDCl_3$)/ppm, δ =11.0, 14.0, 17.7, 22.9, 23.7, 28.9, 30.3, 30.9, 34.3, 36.2, 38.7, 46.4, 65.5, 67.3, 124.7, 130.8, 135.9, 152.2, 172.7, 172.9; Found $[M+H]^+$ ($C_{47}H_{75}O_8$) m/z = 767.5462 (Calc. 767.5462); IR (ATR) *v*/cm^{-1}: 3644, 2957, 1734, 1435, 1135, 756.

*2.2.9. Preparation of second generation tetraphenol (**11**)*

3-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)propanoic acid **9** (4.36 g, 15.67 mmol), second generation hydroxyl linker **6** (1.50 g, 3.13 mmol), DPTS (60%) and DCC (3.23 g, 15.67 mmol) were allowed to react according to the general esterification method. The crude product was purified by flash column chromatography on silica eluting with hexane/ethyl acetate (90:10) (R_f = 0.13) to afford **11** as a colourless glassy solid (3.39 g, 72%); Mp (42-45 °C); ^{1}H NMR (400 MHz/$CDCl_3$)/ppm, δ = 0.87 (m, 6H, -CH_3), 1.13 (s, 6H, -CH_3), 1.22 (s, 3H, -CH_3), 1.31 (m, 8H, -CH_2), 1.42 (s, 72H, -CH_3), 1.57 (m, 1H, -CH), 2.59 (t, 2H, *J* = 16 Hz, -CH_2), 2.83 (t, 2H, *J* = 16 Hz, -CH_2), 4.01 (m, 2H, -CH_2), 4.18 (s (br), 8H, -CH_2), 4.25 (s (br), 4H, -CH_2), 5.06 (s, 4H, -OH), 6.98 (s, 8H, -ArCH); ^{13}C NMR (100 MHz/$CDCl_3$)/ppm, δ = 11.0, 14.0, 17.7, 18.2,

22.9, 23.7, 28.9, 30.3, 30.9, 34.3, 36.2, 38.7, 46.4, 65.1, 65.7, 67.7, 124.7, 130.8, 135.9, 152.2, 172.0, 172.6; Found $[M+Na]^+$ ($C_{91}H_{138}O_{18}$) m/z = 1541.9775 (Calc. 1541.9883); IR (ATR) *v*/cm^{-1}: 3646, 2958, 1739, 1435, 1121.

*2.2.10. Preparation of third generation octaphenol (**12**)*

3-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)propanoic acid **9** (1.48 g, 5.30 mmol), third generation hydroxyl linker **8** (0.50 g, 0.53 mmol), DPTS (60%) and DCC (1.09 g, 5.30 mmol) were allowed to react according to the general esterification method with the exception of dimethylacetamide which was used as the solvent (30 mL). The crude reaction was purified by precipitation into water followed by the general washing procedure and flash column chromatography on silica eluting with chloroform/methanol (99.5:0.5) to afford **12** as a white waxy solid (0.24 g, 15%); ^{1}H NMR (400 MHz/$CDCl_3$)/ppm, δ = 0.85 (m, 6H, -CH_3), 1.13 (s, 12H, -CH_3), 1.21 (s, 6H, -CH_3), 1.26 (s, 11H, -CH_2), 1.41 (s, 142H, *tert*-butyl -CH_3), 1.54 (m, 1H, -CH), 2.59 (t, 2H, *J* = 16 Hz, -CH_2), 2.83 (t, 2H, *J* = 16 Hz, -CH_2), 4.18 (m, 2H, -CH_2), 4.22 (m, 28H, -CH_2), 5.06 (s, 8H, -OH), 6.97 (s, 16H, -ArCH). ^{13}C NMR (100 MHz/$CDCl_3$)/ppm, δ = 10.9, 14.1, 17.7, 22.9, 30.3, 30.8, 34.3, 36.1, 46.4, 65.0, 124.7, 130.8, 135.9, 152.2, 171.9, 172.5. Found $[M+Na]^+$ ($C_{179}H_{266}O_{38}$) m/z = 3046.8690 (Calc. 3046.8882); IR (ATR) *v*/cm^{-1}: 3640, 2954, 1736, 1435, 1120.

2.3. General procedure for thermal and oxidative analysis

Thermogravimetric analysis (TGA) was performed using a TA instrument TGA 2950. TGA was carried out under a nitrogen atmosphere from ambient temperature to 500 °C at a rate of 10 °C/min using a sample of approximately 10 mg. Pressurised differential scanning calorimetry (PDSC) was carried out at the BP Technology Centre, Pangbourne. Oxidation induction time (OIT) was performed using a TA instrument Q10 (0010-0141) or Q20 (0020P-0137). The industry standard CEC L 085-99 method was followed whereby 2 mg of sample

was added to an aluminium crucible. The cell was pressurised to 100 psi with cylinder air and the temperature was raised to 50 °C and held isothermally for 5 minutes. The temperature was then ramped at 20 °C/min to 210 °C and held isothermally until the oxidation of the sample was induced. The time of onset of the exotherm minus the time taken to reach 210 °C was reported. PDSC oxidation onset temperature (OOT) was performed using a TA instrument 2910. An in-house method was used whereby 0.5 mg of sample was added to an aluminium crucible. The cell was pressurised to 500 psi with cylinder air with a flow of 60 mL/min. The temperature was raised to 50 °C and was allowed to stabilise before heating at 50 °C/min to 350 °C. The temperature at which the oxidation exotherm occurred was reported.

3. Results and discussion

3.1. Synthesis of dendritic antioxidants

The synthetic route used to produce the first generation hydroxyl linker **4** is shown in Scheme 1, where the first step involved protection of the 1,3-diol moiety of *bis*(MPA) **1** with an acetonide group and was achieved by reacting **1** with 2,2-dimethoxypropane (DMP) in the presence of catalytic amount of *p*-toluene sulfonic acid (TsOH). Esterification of **2** using *N,N'*-dicyclohexylcarbodiimide (DCC) as the coupling agent and 4-(dimethylamino)pyridinium-4-toluenesulfonate (DPTS) as an esterification catalyst were employed for the synthesis of **3** and all subsequent esterifications. [33] To yield the first generation hydroxyl linker **4**, the acetonide group was removed by stirring the protected diol **3** in methanol in the presence of an acidic Dowex resin. Higher generation hydroxyl terminated polyesters were synthesised using the same protection and deprotection strategy as outlined in Scheme 1. A DCC mediated coupling between **4** and **2** was employed in the synthesis of the diacetonide triester **5** and this was deprotected to yield the second generation linker **6**. The third generation hydroxyl linker **8** was synthesised according to the synthetic protocol shown in Scheme 1,

where a DCC mediated coupling was first employed in the synthesis of **7** followed by deprotection of the acetonide protecting groups in order to afford the desired polyol **8** in 79% yield. The antioxidant functionality was then introduced in a divergent approach utilising the proven DCC mediated coupling route (Scheme 2) to obtain the desired diphenol **10**. The sterically hindered phenol 3-(3,5-di-*tert*-butyl-4-hydroxy-phenyl)-propionic acid **9** was chosen as the terminal unit to provide antioxidant functionality onto the hydroxyl linkers of the *bis*(MPA)-based ester dendrons for several reasons. The acid moiety of **9** render it suitable for DCC esterification which had proved effective in this synthetic study and the ethyl linker between the aromatic ring and the acidic functionality serves to aid the solubility of the branched antioxidants in a hydrocarbon-based medium. The second and third generation polyester hydroxyl linkers (Figure 3) were subjected to the same synthetic procedure as described for the first generation ester that afforded the tetra- **11** and octa- **12** phenolic esters in 72% and 15% yields, respectively. The third generation octaphenol **12**, however, required the use of an alternative solvent, dimethylacetamide, to overcome the insolubility of the third generation hydroxyl linker. In addition, purification of **12** also proved to be more challenging with initial precipitation into water to remove the dimethylacetamide, followed by dissolution in dichloromethane and multiple washings with sodium hydroxide to remove the excess **9** that had been used. Flash column chromatography was then employed twice to remove traces of the *N,N'*-dicyclohexylurea (DCU) by-product from the esterification process. The lengthy purification process suggested that impurities and solvent were easily trapped within the large structure of the compound **12** and such phenomenon within dendritic structures has been reported previously by Meijer and co-workers. [34,35] The low yield of the octaphenol **12** can be attributed to the steric congestion of the hydroxyl end groups in the third generation hydroxyl linker **8**, which inhibits the desired coupling. For spectroscopic data of these branched materials, please refer to the Supporting Information (SI).

3.2. Thermal stability studies

TGA was used to investigate the thermal stability characteristics of the synthesised antioxidants **10-12**. The thermal stability of the diphenol **10** was compared to three commercial antioxidants, BHT, Irganox L135 and Irganox L57 (Figure 4). As shown in Figure 5, the thermal stability of **10** was significantly higher when compared to BHT and examination of molecular weight alone revealed that BHT (M_w = 220.36) was nearly 4 times smaller than **9** (Mw = 767.10) indicating that it was much more susceptible to volatilisation, hence complete consumption was seen at *ca.* 150 °C. The first generation diphenol **10** also revealed a thermal stability of *ca*. 100 °C higher than both Irganox L135 (Average Mw = 390.61) and L57 (Average Mw = 337.55). Again, these results confirmed that the higher molecular weight of **10** was contributing to the observed enhanced thermal stability properties. The thermal stability of polyphenols **11** and **12** were also analysed and revealed a one-step degradation, other than loss of residual entrapped solvent (*ca*. 10%) at *ca.* 100 °C as shown in Figure 6. A slight increase in the stability was observed between each generation, most likely as a result of increased bulkiness. [30] TGA results confirmed that the design of these novel dendritic compounds had successfully resulted in increasing the bulkiness, thus reducing the effect of physical loss of the antioxidant through volatilisation. It is not unreasonable to thus assume that these new branched antioxidants will be present in hydrocarbon media for an increased period of time at elevated temperatures in relation to the lower molecular weight systems and will consequently provide prolonged stability to the bulk phase.

3.3. Oxidative stability studies

To further assess the antioxidant potential, **10-12** were blended into a synthetic lubricant base oil - Durasyn 164 (a polyalphaolefin, hydrogenated hydrocarbon base oil composed of dec-1-ene trimers typically used in lubricating oils). At this stage it was found that both the first generation **10** and second generation **11** were soluble in the hydrocarbon, however, the third

generation **12** was insoluble and hence analysis of this polyphenol **12** proved to be unfeasible. The commercial antioxidants Irganox L135 and Irganox L57 were once again used as a comparison and samples were prepared by blending of 0.5% w/w of each antioxidant in 50 mL of lubricant base oil. The blends were analysed using PDSC to monitor the heat effects associated with phase transitions and chemical reactions as a function of temperature. Oxidation induction time (OIT) and oxidation onset temperature (OOT) were used to investigate the effect of antioxidants on the stability of an oil sample. OIT revealed that the presence of **10** and **11** in the base oil had resulted in significant increase in the stability of the sample (*ca*. 229%) as shown in Figure 7. The induction time was increased from < 3 minutes for the unblended base oil to *ca.* 12 minutes for the blended samples. In addition, **10** and **11** showed superior performance to both commercial antioxidants, Irganox L135 and Irganox L57. To further investigate the properties of these antioxidants, a normalisation test was carried out where additional blends were generated with respect to the number of moles of Irganox L135 which possesses only one active phenolic group. The number of moles of the first and second generation were then either halved or quartered corresponding to their respective 2 and 4 active phenolic groups (Table 1).

The results from these blends shown in Figure 8 were very promising and revealed that even though there was a slight drop in induction time, the dendrons **10** and **11** still performed much better than Irganox L135. The OOT results for each oil blend are presented in Figure 9 where again, a significant increase in temperature was observed when **10** and **11** were incorporated into the blend when compared to the base oil in isolation. The above results indicated that the onset of oxidation of a hydrocarbon matrix can be delayed using **10** and **11** and that these additives not only provide increased oxidative stability but also enhances the performance of the bulk matrix at higher temperatures.

4. Conclusions

In summary, we report a divergent synthetic approach to develop a series of novel antioxidant terminated polyester dendrons (3 different generations) using 2,2-bis(hydroxymethyl)propionic acid (bis(MPA)) as the branching unit to enhance solubility and sterically hindered phenol 3-(3,5-di-*tert*-butyl-4-hydroxy-phenyl)-propionic acid to provide antioxidant functionality. The antioxidant dendrons **10** and **11** (first and second generations, respectively) were scaled up successfully to 100 g and the thermal stability, assessed by thermogravimetric analysis, revealed that all the functionalised dendrons (**10**, **11** and **12**) have enhanced (*ca.* 100 °C higher) thermal stability when compared to BHT, Irganox L135 and Irganox L57. Antioxidant ability was evaluated using pressurised differential scanning calorimetry and when blended with a lubricant base oil, at 0.5% w/w, an increase in antioxidant performance was observed for dendrons **10** and **11** when compared to BHT, Irganox L135 and most promisingly the high temperature antioxidant Irganox L57. These results confirmed that the onset of oxidation of a hydrocarbon matrix can be delayed using the dendritic antioxidants. This study revealed that encouragingly these antioxidant dendritic additives provide not only increased oxidative stability of hydrocarbon matrices for longer time periods but also serve to enhance their performance at higher temperatures.

Acknowledgements

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Data Availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations. Processed data can be found in the associated Supporting Information file.

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Figures and schemes captions

Figure 1. Proposed mechanism of radical scavenging of BHT.

Figure Error! No text of specified style in document.**.** Examples of synthetic and natural phenolic antioxidants: BHT, 4,4'-methylene*bis*(2,6-*di*-*tert*-butylphenol) and α-tocopherol from vitamin E.

Scheme 1. Synthesis of the first generation hydroxyl linker **4** based upon bis(MPA). Second and third generation polyester hydroxyl linker **6** and **8** were synthesised using the same protection, esterification and deprotection strategy.

Scheme 2. Attachment of antioxidant functionality to the first generation hydroxyl linker.

Figure 3. Structures of the second generation (**11**) and third generation (**12**) antioxidants, respectively.

Figure 4. Commercial antioxidants **13**) Irganox L135 and **14**) Irganox L57.

Figure 5. Thermogravimetric analysis of **10** when compared to BHT, Irganox L135 and Irganox L57.

Figure 6. Thermogravimetric analysis of polyphenol dendrons **10, 11 and 12.**

Figure 7. Average Oxidation Induction Time of 0.5% w/w antioxidant-base oil samples run in duplicate.

Table 1. Calculations to determine amount of **10** and **11** required when compared to Irganox L135.

Figure 8. Average Oxidation induction time comparison of w/w and mol% oil blends run in duplicate.

Figure 9 Average Oxidation Onset Temperature of 0.5% w/w antioxidant-base oil samples run in duplicate.

Figures and Schemes

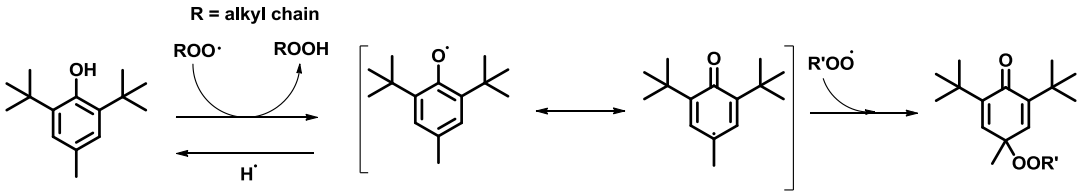
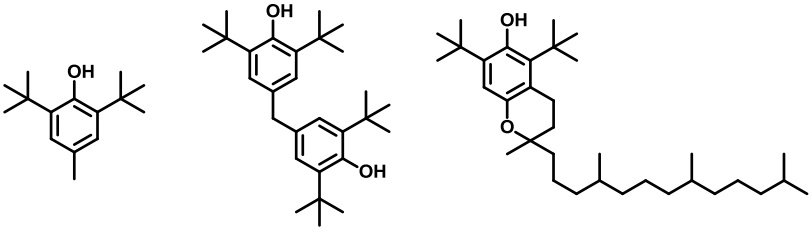


Figure 1



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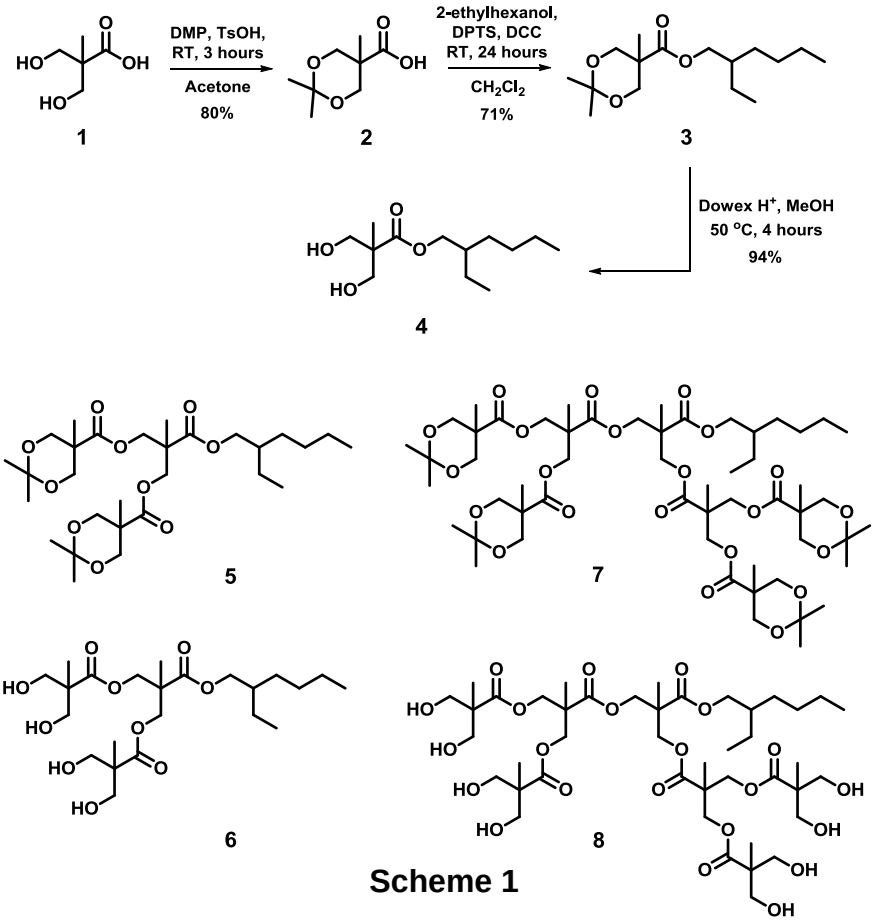
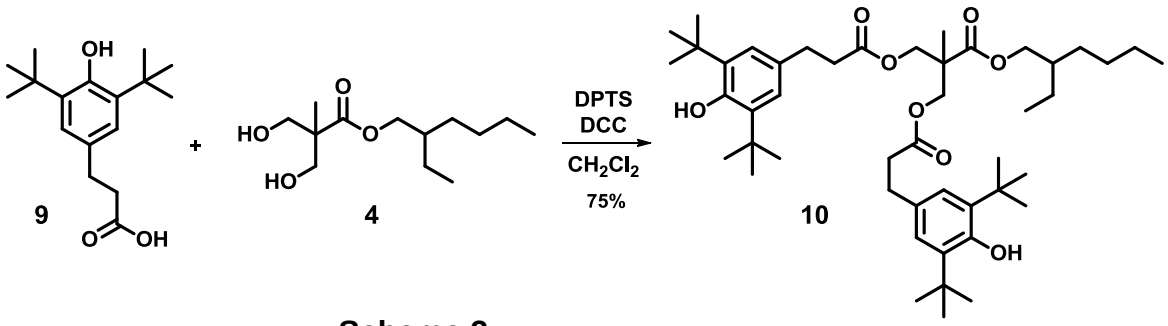


Scheme 1



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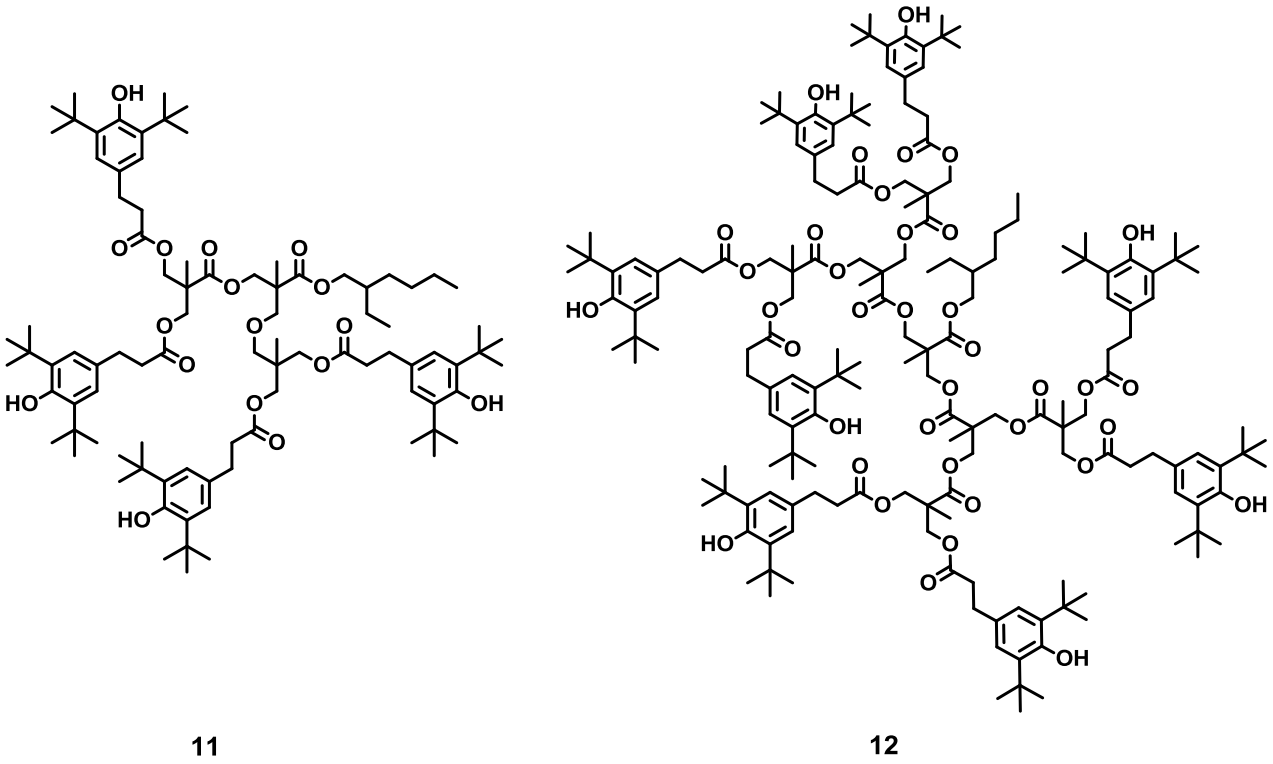
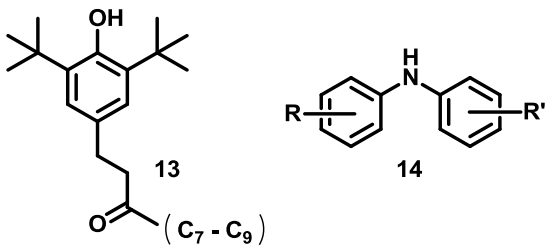


Figure 3



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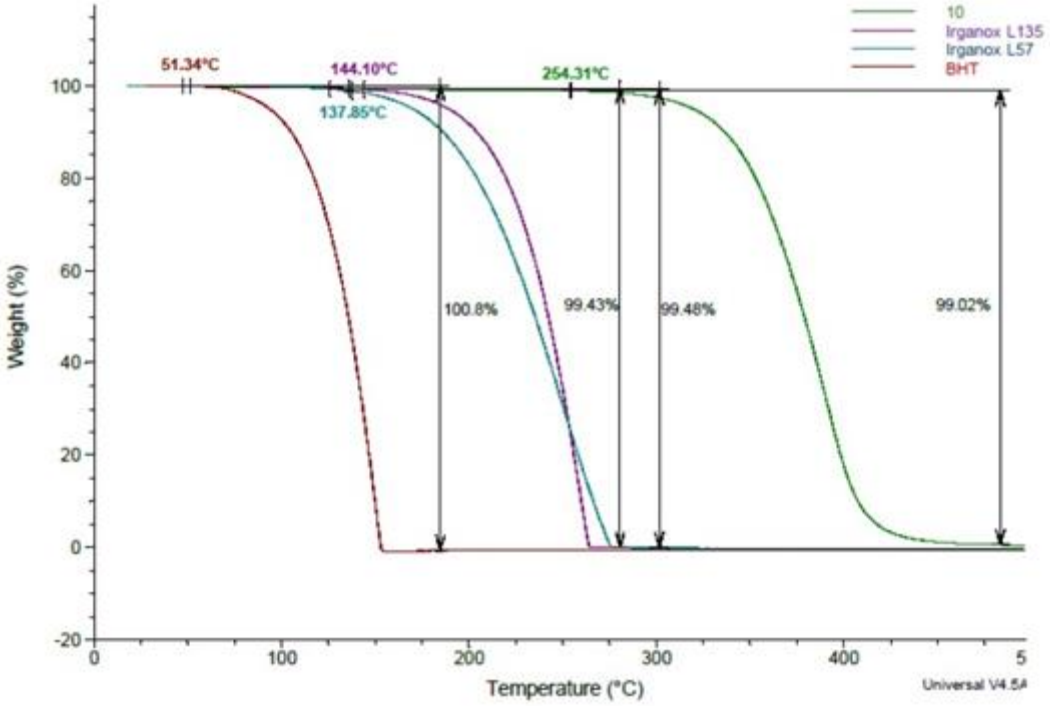

Figure 5

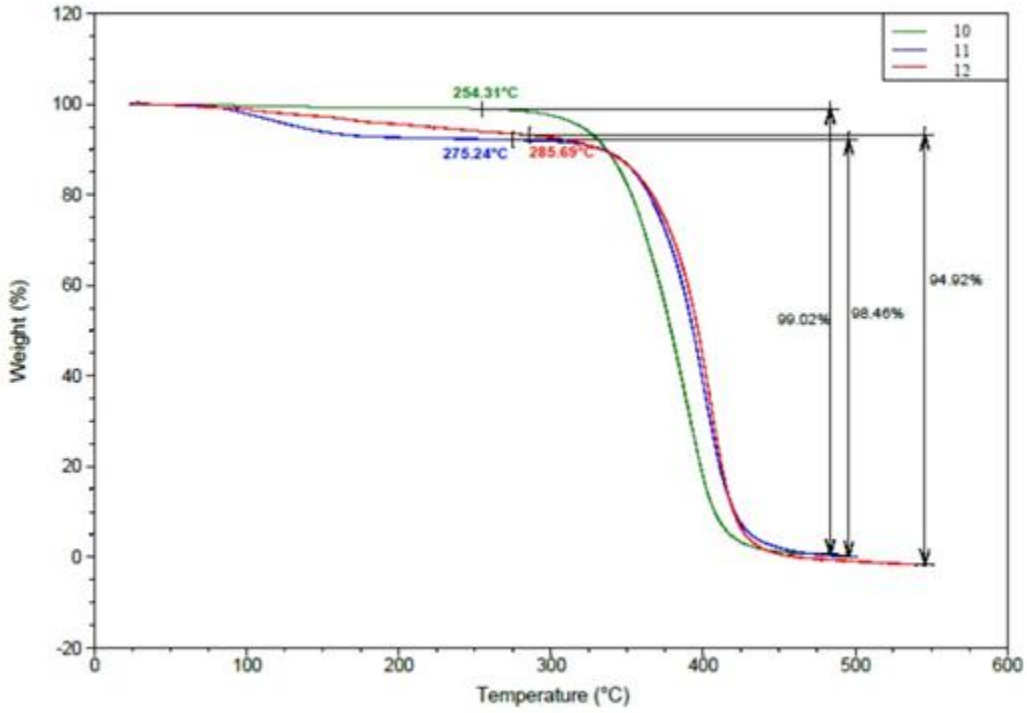

Figure 6

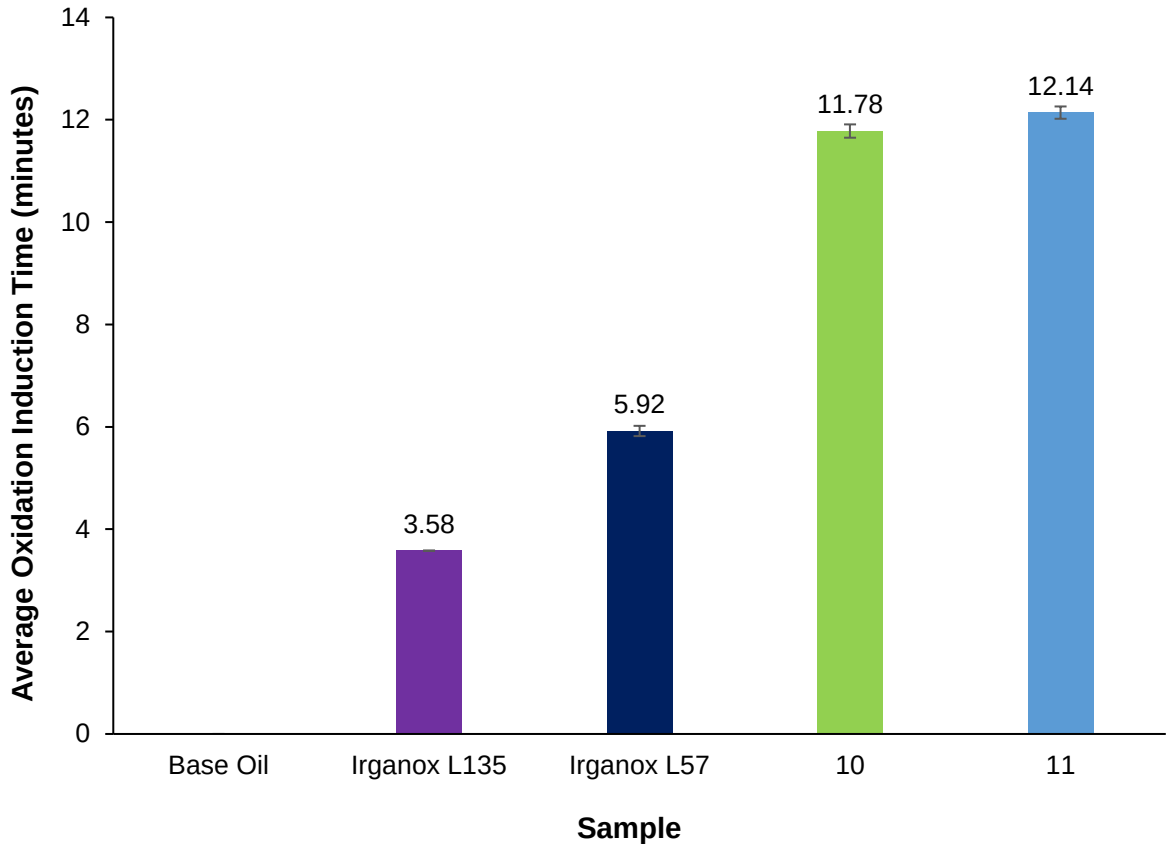

Figure 7

Sample	Mw	Number of phenolic functionalities	Number of mmols	Mass required for the oil blend
Irganox L135	390.61	1	0.64	0.2500 g
10	767.09	2	0.32	0.2455 g
11	1506.08	4	0.16	0.2410 g

Table 1

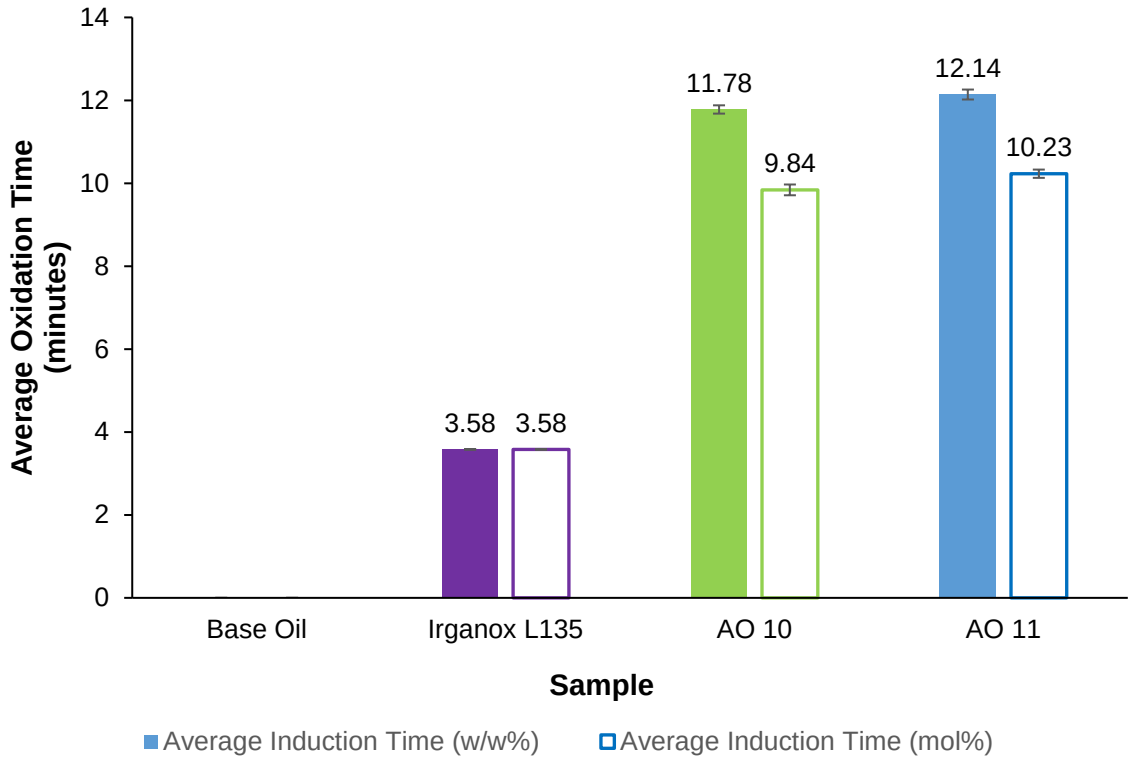

Figure 8

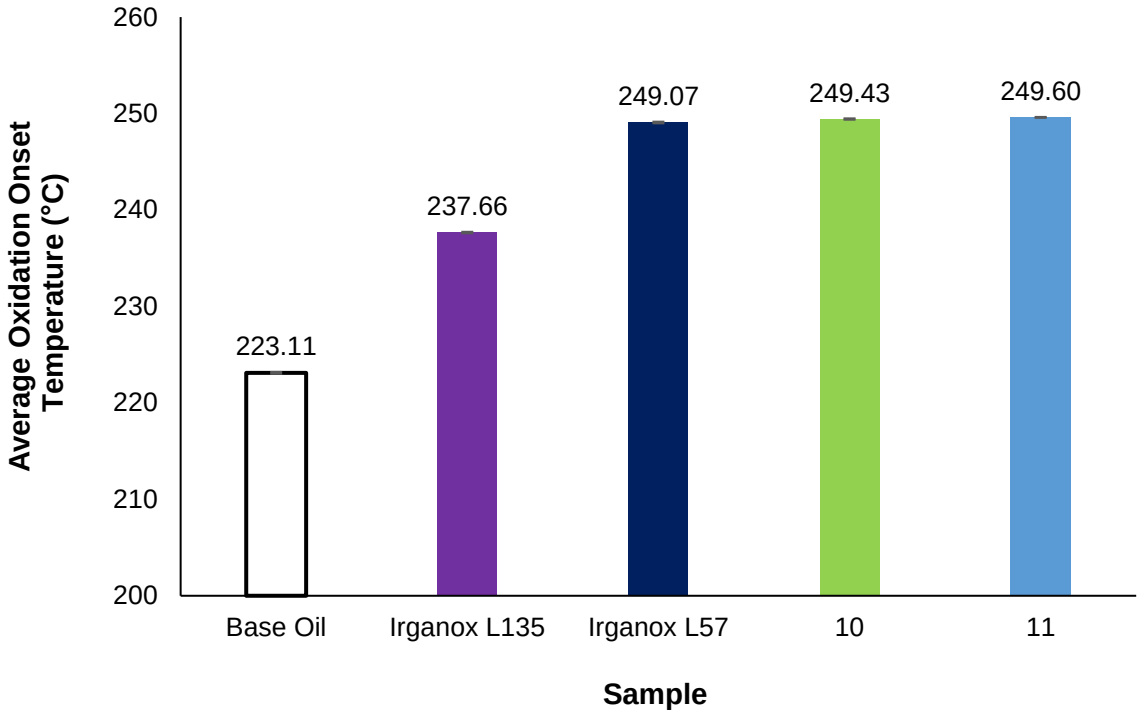

Figure 9