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Fullerene C₆₀ conjugated with phenols as new hybrid antioxidants to improve the oxidative stability of polymers at elevated temperatures†

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Four derivatives of fullerene C₆₀ with covalently bonded simple phenols were tested as inhibitors of oxidation of polyethylene at elevated temperatures 150–250 °C under non-isothermal conditions. Temperatures of the start of oxidation as well as the Arrhenius kinetic parameters of overall oxidation indicate a significant improvement of the oxidative stability of composites with fullerene derivatives.

Introduction

Several types of substances can be applied to enhance the oxidative stability of polymers, plastics, resins and lubricants, but the most commonly used include phenolic, amine and organosulfur derivatives¹ as chain-breaking antioxidants, *i.e.* molecules able to trap peroxy radicals mediating the autoxidation.² Their effectiveness depends on the mechanism of inhibition (for example, H atom abstraction as a one- or multiple step process),^{3–6} the reactivity of secondary products formed from antioxidants,⁷ the type of material to be stabilized, the conditions of usage and the amount of the antioxidant in the polymer or the lubricant.^{8,9} It is important to obtain a good match between the reactivity of an antioxidant and the nature of the oxidation process with respect to applicability and exploitation conditions of the material to be protected. For example, some kinds of high-performance plastics are applied at high temperature (thermal or electrical insulators, bearings and seals), however most of the antioxidants are characterized by a relatively high volatility, making them difficult to be used at temperatures above 100 °C.^{10,11} Under such conditions typical “food antioxidants” are not effective and at higher temperatures they may be a source of re-initiation of the autoxidation process. On the other side, amines and organosulfur antioxidants produce sulphur or nitrogen oxides that can cause corrosion of metal parts. Another negative effect is a migration of the antioxidant or other additives from the plastic material into the liquid, food or medicines. This process depends on concentration of a substance in polymer matrix, temperature, and the time of interfacial contact¹² and it has been found¹³ that common

antioxidants like 2,6-di-*tert*-butyl-4-methylphenol (BHT), 2,6-di-*tert*-butyl-4-methoxyphenol (BHA) or Irganox 1330 can migrate from polymer into aqueous/oil at 40 °C during several days, and the process is faster as the fat content of food increases.¹⁴ Therefore, an ideal antioxidant for polymers, lubricants and resins should be active, non-volatile, and not corrosive. Another important feature of a potent antioxidant able to break the oxidative destruction of polymers is ability to react not only with peroxy radicals (usual chain mediators of low temperature peroxidation) but also to scavenge other, non-peroxy radical intermediates responsible for propagation of kinetic chain. Recent works suggest that high temperature oxidative degradation of polymers proceeds with participation of wide variety of radicals with alkoxy radicals from decomposition of tetraoxides (non Russell termination products).^{15,16}

There are a few reports concerning the pristine fullerene C₆₀ or its derivatives as a scavenger of several kinds of radicals. The carbon sphere of C₆₀ is thermally stable (up to 600 °C),¹⁷ traps several radicals,^{18–20} and, therefore, is a good starting structure for development of new radical-scavengers to be used as stabilizing agents during thermal oxidation. We described the antioxidant behaviour of C₆₀ during the autoxidation of stearic acid (STA) over a wide range of temperatures, as a non-corrosive agent effectively increasing the oxidative stability of lubricants.²¹ For high temperature oxidation of STA, the phenolic conjugates of C₆₀ are more active antioxidants than the pristine C₆₀ and phenols used alone.²² This lead us to hypothesis that conjugates of C₆₀ with phenols are good candidates for hybrid antioxidants to be used in polymers at temperatures above 100 °C. Herein we present experimental study in which kinetic parameters of thermo-oxidation of pure high density polyethylene (HDPE) were determined and compared with kinetic parameters of HDPE containing pristine fullerene C₆₀ and C₆₀ adducts with four phenols I–IV (see Chart 1) at concentration 0.065–1%.

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† Electronic supplementary information (ESI) available: Recorded DSC curves, plots of eqn (1) ($\log \beta$ versus $1000/T_c$), tables with statistical and kinetic parameters, and experimental procedures. See DOI: 10.1039/c7ra08764k



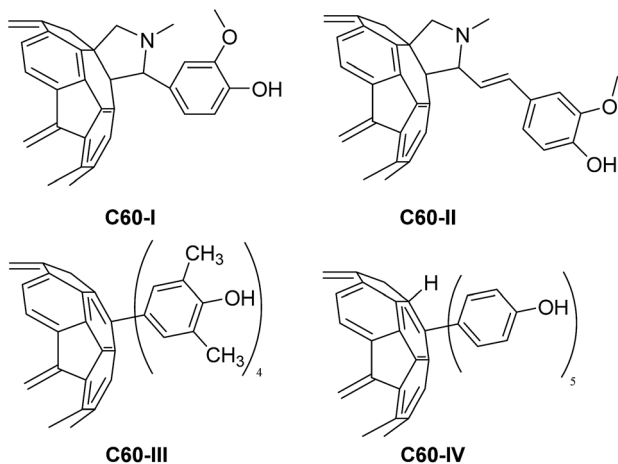


Chart 1 Structures of fullerene C₆₀ derivatives: *N*-methyl-2-[4-hydroxy-3-methoxyphenyl]-3,4-[60]fulleropyrrolidine (C₆₀-I), *N*-methyl-2-[2-(4-hydroxy-3-methoxyphenyl)vinyl]-3,4-[60]fulleropyrrolidine (C₆₀-II), tetra-2,6-methyl-4-hydroxyphenyl[60]fullerene (C₆₀-III), and penta-(4-hydroxyphenyl)-hydro[60]fullerene (C₆₀-IV). Synthesis and characterization of C₆₀ derivatives is described in ref. 22, and quoted in ESI.†

Experimental

Synthesis of C₆₀(I–IV) is described in ref. 22 see also ESI.† Thermal stability of obtained C₆₀ derivatives was measured using a thermogravimeter (TA Q50) with platinum vessels under nitrogen flow. Samples of fullerene C₆₀ derivatives C₆₀(I–IV) were dried in vacuum in 40 °C for 12 h. In a typical TG measurement a sample (6–7 mg) was heated at 5 K min⁻¹ from 50 to 600 °C. Universal V4.54 TA Instruments software was used for data collection and analysis.

Du Pont 910 apparatus with Du Pont 9900 thermal analyzer and normal pressure cell was used. Experiments were performed under oxygen flow 6 dm³ h⁻¹ in open aluminum pans with an empty aluminum pan used as a reference. Samples (3.1–3.8 mg) of HDPE or HDPE with additives were heated from 50 to 250 °C with linear heating rate β . Preparation of samples: HDPE (0.10 ± 0.01 g) was crushed in a mortar then calculated mass of pristine fullerene C₆₀ or its derivative (Chart 1) and a few mL of CS₂ was added with continuous grinding of the mixture until the homogeneous powder was obtained. The composite was moved into a glass vial and left for one hour to evaporate CS₂. More information can be found in ESI.†

Results and discussion

Thermal effect of oxidation can be recorded as the heat flow *versus* temperature and we employed Differential Scanning Calorimetry (DSC) for monitoring the oxidation process in non-isothermal mode. Typical DSC curves for oxidation of HDPE containing 1% w/w C₆₀-I for different β (2.5–20.0 K min⁻¹) are shown in Fig. 1. In general, the oxidative stability can be expressed as the length of the lag phase from start of experiment to the moment when thermal effect of spontaneous

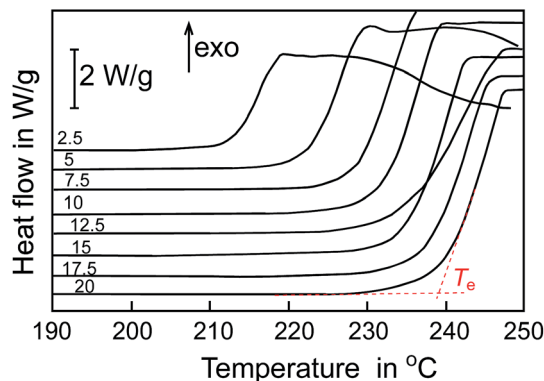


Fig. 1 DSC curves (obtained for heating rates 2.5–20 K min⁻¹, indicated as numbers above each curve, the curves were shifted vertically for clarity) of oxidative decomposition of HDPE containing: 1% w/w of *N*-methyl-2-[4-hydroxy-3-methoxyphenyl]-3,4-[60]fulleropyrrolidine, C₆₀-I. The example of the extrapolated temperature of the start of oxidation (T_e) is indicated.

oxidation is detected. In non-isothermal DSC method the temperature is a linear function of time, thus, a temperature of start of oxidation (T_e, in °C) can be easily determined instead of time. Fig. 2 presents T_e values for HDPE containing C₆₀ and its derivatives C₆₀(I–IV) at concentration range 0.065–1% w/w. Indeed, when unsubstituted C₆₀ or compounds C₆₀(I–IV) are present in the polymer, T_e is shifted to higher temperatures and a magnitude of such shift is non-linearly proportional to concentration of the additive.

Addition of small amount of pristine fullerene C₆₀ (0.065%) did not improve the oxidation stability while at concentration higher than 0.125% the parameter T_e increases, see Fig. 2. A similar increase can be observed when conjugates C₆₀(I–IV) are added to HDPE: the values of T_e for HDPE with additives are about 30–40 degrees higher than T_e for pure HDPE (for $\beta = 2.5$ K min⁻¹ a difference is 32 °C, for $\beta = 10$ K min⁻¹ the difference is 37 °C).

In our previous publications^{21,23,24} we interpreted the shape of DSC curves of thermal effect of lipids and hydrocarbons oxidation and we proved that T_e parameter corresponds to constant degree of conversion (start of oxidation). Therefore,

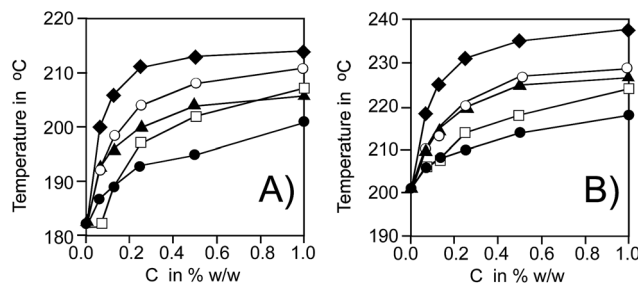


Fig. 2 Comparison of the extrapolated temperature of start for oxidation T_e (in °C) obtained for HDPE containing: pristine C₆₀ (□) and derivatives: C₆₀-I (○), C₆₀-II (▲), C₆₀-III (◆), C₆₀-IV (●) at various concentration (0–1% w/w) at heating rate $\beta = 2.5$ K min⁻¹ (panel A) and at $\beta = 10$ K min⁻¹ (panel B).



T_e collected for series of different β 's (see, for example, Fig. 1) after recalculation into absolute temperature can be used for the calculation of the kinetic parameters of the process by iso-conversional methods. For a series of oxidations carried out with different β a linear correlation of $\log \beta$ with reciprocal of T_e (in kelvins) is found:^{21,23,24}

$$\log \beta = a \times T_e^{-1} + b \quad (1)$$

The slope a and intersection b can be used for calculation of the activation energy (E_a) and pre-exponential factor (Z) from equations proposed by Ozawa and independently, by Flynn and Wall (OFW method):^{25–28}

$$E_a = -2.19R(d \log \beta/dT) \quad (2)$$

$$\log Z = \log(E_a/R) - b - 2.315 \quad (3)$$

where: R – the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$).

Rate constants (k , in min^{-1}) for oxidation were calculated from the Arrhenius equation $k = Z \exp(-E_a/RT)$ for temperatures 50–250 °C.

Table 1 presents the overall Arrhenius kinetic parameters of oxidation of HDPE with and without additives. The activation parameters $E_a = 129 \pm 7 \text{ kJ mol}^{-1}$ and $Z = 1.11 \times 10^{14} \text{ min}^{-1}$ obtained for non-inhibited process (no additives) are in good agreement with $127 \pm 6 \text{ kJ mol}^{-1}$ and $7.15 \times 10^{13} \text{ min}^{-1}$ measured earlier²⁴ as well as with other literature values.^{10,29} The values of activation energy of HDPE oxidation vary with the concentration of the added derivatives. Addition of pristine fullerene C_{60} to HDPE causes the growth of E_a with maximum at 0.5% w/w. Compounds $\text{C}_{60}\text{-II}$ and $\text{C}_{60}\text{-III}$ exhibit maximal value of activation energy (134 ± 6 and $140 \pm 3 \text{ kJ mol}^{-1}$, respectively) at concentration 0.065% w/w, whereas for $\text{C}_{60}\text{-I}$ and $\text{C}_{60}\text{-IV}$ the maximal E_a is observed at concentrations 0.25% and 1%.

E_a and Z can be easily converted into rate constants calculated for given temperature. The values of the overall oxidation rate constant for pure HDPE and for the oxidation of polymer containing C_{60} and its derivatives $\text{C}_{60}\text{-(I–IV)}$ are listed in Table 1 and they confirm the inhibitory properties of studied compounds. As can be seen in Table 1 ($\log k$ for 150 °C) and in Fig. 3 ($\log k$ for 100 and 200 °C), pristine fullerene C_{60} causes a decrease of k 's within the whole range of concentrations (ten-fold decrease in comparison with pure HDPE). When polyethylene sample contains any of the four $\text{C}_{60}\text{-(I–IV)}$ derivatives, the oxidation is slower than oxidation of pure HDPE. The observed stabilizing effect is stronger than for polyethylene containing 0.5% of BHT as a typical antioxidant widely used in polymers: values of $\log(k/\text{min})$ for the oxidation of polyethylene with 0.5% BHT at temp. 100, 150 and 200 °C are: -1.841 , -0.342 , and $+0.868$, respectively (see ref. 24 and Table S27†).

Comparison of the rate constants is more reasonable than comparison of E_a values, in order to eliminate the possible misinterpretation connected with the isokinetic inversion of reaction rates (simple calculations for two processes described by two series of the Arrhenius parameters E_a and Z indicates that at temperatures below the isokinetic temperature, T_{iso} , the

Table 1 Values of the overall activation energy (E_a) and pre-exponential factor (Z), overall rate constants (k , at 150 °C) for oxidation of pure HDPE and HDPE containing fullerene C_{60} and its derivatives, $\text{C}_{60}\text{-(I–IV)}$ ^a

C^b [% w/w]	E_a^c [kJ mol ⁻¹]	$\log(Z/\text{min}^{-1})$	$\log(k/\text{min}^{-1})$ 150 °C
Pure HDPE			
—	129 ± 7	14.04	-1.83
Fullerene C_{60}			
0.065	127 ± 5	13.85	-1.83
0.125	136 ± 8	14.66	-2.13
0.250	142 ± 8	15.04	-2.45
0.500	161 ± 8	17.06	-2.88
1.000	156 ± 7	16.33	-2.97
Fullerene derivative $\text{C}_{60}\text{-I}$			
0.065	141 ± 5	15.08	-2.28
0.125	142 ± 8	15.04	-2.46
0.250	154 ± 4	16.13	-2.84
0.500	143 ± 4	14.79	-2.85
1.000	142 ± 7	14.65	-2.94
Fullerene derivative $\text{C}_{60}\text{-II}$			
0.065	134 ± 6	14.35	-2.23
0.125	131 ± 4	13.83	-2.32
0.250	124 ± 5	12.99	-2.37
0.500	124 ± 3	12.81	-2.49
1.000	126 ± 3	12.95	-2.59
Fullerene derivative $\text{C}_{60}\text{-III}$			
0.065	140 ± 3	14.77	-2.56
0.125	132 ± 3	13.66	-2.64
0.250	128 ± 7	13.09	-2.74
0.500	130 ± 7	14.12	-2.87
1.000	120 ± 5	12.07	-2.75
Fullerene derivative $\text{C}_{60}\text{-IV}$			
0.065	129 ± 5	13.89	-2.00
0.125	133 ± 5	14.27	-2.12
0.250	140 ± 3	15.03	-2.28
0.500	142 ± 8	15.09	-2.40
1.000	148 ± 4	15.57	-2.64

^a Full data including statistic and kinetic parameters are given in ESI.

^b Concentration in % w/w. ^c Errors of the activation energy E_a were calculated from the standard deviations of slopes calculated for confidence level 90%.

process with higher E_a is slower whereas at temp. above T_{iso} the process with higher E_a proceeds faster).^{22,24} For example, oxidation of polyethylene inhibited by 1% $\text{C}_{60}\text{-III}$ is described by $E_a = 120 \text{ kJ mol}^{-1}$ and $Z = 1.2 \times 10^{12} \text{ min}^{-1}$, giving the rate constants $1.85 \times 10^{-5} \text{ min}^{-1}$ at 100 °C and 0.066 min^{-1} at 200 °C. If 1% $\text{C}_{60}\text{-IV}$ is used, the kinetic parameters $E_a = 148 \text{ kJ mol}^{-1}$ and $Z = 3.7 \times 10^{15} \text{ min}^{-1}$ allow to calculate $k_{100^\circ\text{C}} = 8.38 \times 10^{-6} \text{ min}^{-1}$ and $k_{200^\circ\text{C}} = 0.193 \text{ min}^{-1}$. Thus, at 100 °C $\text{C}_{60}\text{-IV}$ is more active than $\text{C}_{60}\text{-III}$ whereas at 200 °C the derivative $\text{C}_{60}\text{-III}$ is more active than $\text{C}_{60}\text{-IV}$. For this particular pair of kinetic parameters $T_{\text{iso}} = \Delta E_a / (8.314 \times \Delta \ln Z) = 145 \text{ °C}$ and indeed, rate constants presented in Table 1 for 150 °C are almost the same for $\text{C}_{60}\text{-III}$ and for $\text{C}_{60}\text{-IV}$. Such inversions of the



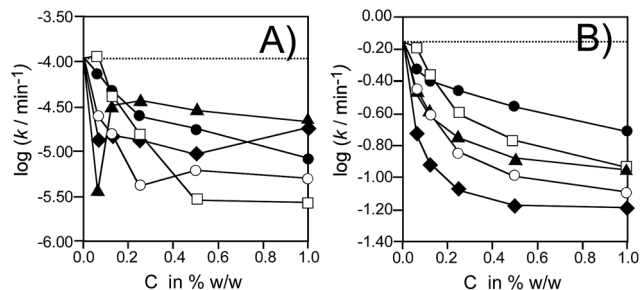


Fig. 3 Comparison of the log k for the oxidation of HDPE (dashed line) and HDPE containing: pristine C_{60} (\square) and derivatives: C_{60} -I (\circ), C_{60} -II (\blacktriangle), C_{60} -III (\blacklozenge), C_{60} -IV (\bullet) at temperature 100 °C (panel A) and 200 °C (panel B). Rate constants were calculated from E_a and Z parameters listed in Table 1.

rates of the oxidation can be clearly observed if the results shown in Fig. 3A are compared with results presented in Fig. 3B: the rates in Fig. 3A are calculated below T_{iso} while Fig. 3B presents the results calculated above T_{iso} . This apparent discrepancy creates awareness and understanding of the kinetic behaviour of the systems monitored at various temperatures.

As can be seen in Fig. 3B, first three derivatives (C_{60} with I, II, III) exhibit significantly better activity than C_{60} -IV. Perhaps, the differences in phenolic O–H bond strength are the main reason responsible for this effect. C_{60} -I and C_{60} -II contain *ortho*-methoxyphenol moiety, C_{60} -III contain *o,o*-dimethylphenol moiety, whereas the phenol residues in C_{60} -IV contain non-hindered hydroxyl groups. The Bond Dissociation Enthalpies (BDE) for O–H in the series:³⁰ phenol, 2,6-dimethoxyphenol, ‡ 2,6-dimethylphenol are: 88.3, 83.2, and 84.5 kcal mol⁻¹, respectively, with the highest BDE for unsubstituted phenol, that will be the worse H-atom donating agent within this series. Therefore, among all four derivatives, the derivative C_{60} -IV exhibits the weakest synergy of phenolic component (H-atom donor to a radical) and C_{60} moiety (being a scavenger able to form the adducts with non-peroxyl radicals).

We also determined thermal stability (volatility) of the obtained conjugates and compared with volatility of low molecular phenolic antioxidants BHT and 2,2,5,7,8-pentamethyl-6-hydroxyschromanol (PMHC). On the basis of thermogravimetric curves presented in Fig. 4 it can be stated that the conjugates of C_{60} (with exception of C_{60} -III) are not volatile and they are thermally stable below 300 °C, in contrast to simple phenols that completely evaporate at temperatures below 180 °C.

Combined TG and DSC result demonstrate that at temperatures corresponding to T_e (180–240 °C) the additives C_{60} -I, C_{60} -II and C_{60} -IV are still present within the polymer and they are responsible for increase of the oxidative stability of the system. The exception is C_{60} -III, that is less stable. However, the antioxidant effect of C_{60} -III is also significant and we suppose this

‡ Those experimental BDE values were taken from one series of EPR equilibration studies from ref. 30 For mono-*ortho*-MeO-phenol BDE(O–H) is 86 or 84 kcal mol⁻¹, available in Luo: *Comprehensive handbook of bond dissociation energies*, CRC Press, 2007.

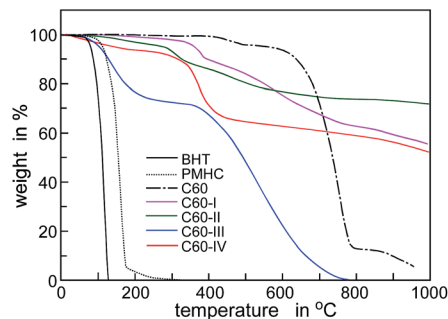


Fig. 4 Thermogravimetric curves of C_{60} and its derivatives C_{60} -I-IV and common antioxidants: 2,6-di-*tert*-butyl-4-methylphenol (BHT) and 2,2,5,7,8-pentamethyl-6-hydroxyschromane (PMHC) recorded for the heating rate $\beta = 5 \text{ K min}^{-1}$.

compound decomposes to the products able to enhance the oxidative stability of the whole system.

Earlier experimental results indicated that C_{60} does not exhibit antioxidant properties in such model systems as unsaturated hydrocarbons in air-saturated solution at moderate temperatures (30 °C in chlorobenzene, oxidation initiated with azobisisobutyronitrile)³¹ suggesting rather weak reactivity of fullerene toward peroxyl radicals: rate constant of reaction of C_{60} with cumylperoxyl radicals, $(3.1 \pm 1.1) \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$,³¹ is extremely slow comparing to rate constant $(2.0 \pm 0.8) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for reaction with cumyl radicals.^{20,32} Another explanation of different behavior of fullerene in saturated and unsaturated hydrocarbons was discussed in our previous work as an effect of different ratio of rate constant of two competitive processes: chain-breaking (k_{inh}) and chain propagation (k_p). Depending on the k_p for propagation of lipid or hydrocarbon, the same molecule can behave as a good antioxidant in hydrocarbon ($k_{inh}/k_p > 1000$) but with no antioxidant activity (no induction period will be observed) in unsaturated hydrocarbon ($k_{inh}/k_p \ll 1000$).²²

Additional explanation of good antioxidant behaviour of the studied conjugates of C_{60} with phenols is that we monitored a real process of oxidation carried out at temperature above 150 °C where some other radical species can effectively mediate the kinetic chain process of propagation step during hydrocarbon autoxidation. We assign this inhibitory effect as a result of low volatility of C_{60} conjugates, ability of phenolic moieties to react with peroxyl radicals and ability of fullerene spheres to react with other radicals like alkoxy, alkyl, hydroxyl radicals as well as singlet oxygen formed during high temperature decomposition of peroxides (including non-Russel type reaction of tetraoxides).^{15,16}

Conclusions

In order to find a new kind of hybrid antioxidants able to protect the polymers against oxidation in broad range of temperatures we tested four derivatives of fullerene C_{60} with covalently bonded simple phenols during non-isothermal oxidation of polyethylene at temperatures 150–250 °C. The fullerene



derivatives exhibit better antioxidant activity than C₆₀ or phenols used alone, thus, increased efficacy of C₆₀-phenol conjugates is a result of a synergy between phenolic residues (reacting with peroxy radicals by H-atom transfer) and C₆₀ moiety (a “radical sponge” responsible for scavenging non-peroxy radicals at elevated temperatures). Our findings implicate that hybrid materials made of fullerene and phenols can be potentially applied as agents increasing oxidative stability of polymers and other hydrocarbon materials (e.g., lubricants) exploited under severe thermal and oxidative conditions.

Conflicts of interest

The authors declare that there are no conflicts to declare.

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Notes and references

- 1 E. T. Denisov and I. V. Khudyakov, *Chem. Rev.*, 1987, **87**, 1313–1357.
- 2 K. U. Ingold and D. A. Pratt, *Chem. Rev.*, 2014, **114**, 9022–9046.
- 3 M. Lucarini and G. F. Pedulli, *Chem. Soc. Rev.*, 2010, **39**, 2106–2119.
- 4 G. Litwinienko and K. U. Ingold, *J. Org. Chem.*, 2003, **68**, 3433–3438.
- 5 G. Litwinienko and K. U. Ingold, *Acc. Chem. Res.*, 2007, **40**, 222–230.
- 6 M. Musialik and G. Litwinienko, *Org. Lett.*, 2005, **7**, 4951–4954.
- 7 V. W. Bowry, K. U. Ingold and R. Stocker, *Biochem. J.*, 1992, **288**, 341–344.
- 8 S. Q. A. Rizvi, *A Comprehensive Review of Lubricant Chemistry, Technology, Selection, and Design*, ASTM International, 2009.
- 9 L. R. Rudnick, *Lubricant Additives: Chemistry and Applications*, CRC Press, 2nd edn, 2009.
- 10 Y. Bolbukh, P. Kuzema, V. Tertykh and I. Laguta, *J. Therm. Anal. Calorim.*, 2008, **94**, 727–736.
- 11 R. Gensler, C. J. G. Plummer, H. H. Kausch, E. Kramer, J. R. Pauquet and H. Zweifel, *Polym. Degrad. Stab.*, 2000, **67**, 195–208.
- 12 K. Bhunia, S. S. Sablani, J. Tang and B. Rasco, *Compr. Rev. Food Sci. Food Saf.*, 2013, **12**, 523–545.
- 13 Y. Gao, Y. Gu and Y. Wei, *J. Agric. Food Chem.*, 2011, **59**, 12982–12989.
- 14 G. Beldi, S. Pastorelli, F. Franchini and C. Simoneau, *Food Addit. Contam., Part A*, 2012, **29**, 836–845.
- 15 R. Lee and M. L. Coote, *Phys. Chem. Chem. Phys.*, 2016, **18**, 24663–24671.
- 16 R. Lee, G. Gryn'ova, K. U. Ingold and M. L. Coote, *Phys. Chem. Chem. Phys.*, 2016, **18**, 23673–23679.
- 17 W. Vogel, *Appl. Phys. A*, 1996, **62**, 295–301.
- 18 P. J. Krusic, E. Wasserman, P. N. Keizer, J. R. Morton and K. F. Preston, *Science*, 1991, **254**, 1183–1185.
- 19 J. R. Morton, F. Negri and K. F. Preston, *Acc. Chem. Res.*, 1998, **31**, 63–69.
- 20 E. B. Zeinalov and G. Kořmehl, *Polym. Degrad. Stab.*, 2001, **71**, 197–202.
- 21 R. Czochara, P. Ziaja, P. Piotrowski, R. Pokrop and G. Litwinienko, *Carbon*, 2012, **50**, 3943–3946.
- 22 R. Czochara, J. Kusio, M. Symonowicz and G. Litwinienko, *Ind. Eng. Chem. Res.*, 2016, **55**, 9887–9894.
- 23 G. Litwinienko and T. Kasprzycka-Guttman, *J. Therm. Anal. Calorim.*, 1998, **54**, 203–210.
- 24 P. Ziaja, K. Jodko-Piorecka, R. Kuzmicz and G. Litwinienko, *Polym. Chem.*, 2012, **3**, 93–95.
- 25 T. Ozawa, *Bull. Chem. Soc. Jpn.*, 1965, **38**, 1881–1886.
- 26 T. Ozawa, *J. Therm. Anal.*, 1970, **2**, 301–324.
- 27 L. A. Wall, S. Straus, J. H. Flynn, D. McIntyre and R. Simha, *J. Phys. Chem.*, 1966, **70**, 53–62.
- 28 G. Litwinienko, A. Daniluk and T. Kasprzycka-Guttman, *Ind. Eng. Chem. Res.*, 2000, **39**, 7–12.
- 29 M. Iring, F. Tüdös, Z. Fodor and T. Kelen, *Polym. Degrad. Stab.*, 1980, **2**, 143–153.
- 30 M. Lucarini, P. Pedrielli, G. F. Pedulli, S. Cabiddu and C. Fattuoni, *J. Org. Chem.*, 1996, **61**, 9259–9263.
- 31 R. F. Enes, A. C. Tomé, J. A. S. Cavaleiro, R. Amorati, M. G. Fumo, G. F. Pedulli and L. Valgimigli, *Chem.-Eur. J.*, 2006, **12**, 4646–4653.
- 32 E. B. Zeynalov, N. S. Allen and N. I. Salmanova, *Polym. Degrad. Stab.*, 2009, **94**, 1183–1189.

