Fullerene C$_{60}$ conjugated with phenols as new hybrid antioxidants to improve the oxidative stability of polymers at elevated temperatures†

R. Czochara, J. Kusio and G. Litwinienko*

Four derivatives of fullerene C$_{60}$ 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 derivatives† as chain-breaking antioxidants, i.e. molecules able to trap peroxyl radicals mediating the autoxidation. Their effectiveness depends on the mechanism of inhibition (for example, H atom abstraction as a one- or multiple step process), the reactivity of secondary products formed from antioxidants, the type of material to be stabilized, the conditions of usage and the amount of the antioxidant in the polymer or the lubricant. 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. 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 contact and it has been found 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. 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 peroxyl radicals (usual chain mediators of low temperature peroxidation) but also to scavenge other, non-peroxyl radical intermediates responsible for the propagation of kinetic chain. Recent works suggest that high temperature oxidative degradation of polymers proceeds with participation of wide variety of radicals with alkoxyl radicals from decomposition of tetraoxides (non Russel termination products).

There are a few reports concerning the pristine fullerene C$_{60}$ or its derivatives as a scavenger of several kinds of radicals. The carbon sphere of C$_{60}$ is thermally stable (up to 600 °C), traps several radicals, 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 C$_{60}$ 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. For high temperature oxidation of STA, the phenolic conjugates of C$_{60}$ are more active antioxidants than the pristine C$_{60}$ and phenols used alone. This lead us to hypothesis that conjugates of C$_{60}$ 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 C$_{60}$ and C$_{60}$ adducts with four phenols I–IV (see Chart 1) at concentration 0.065–1%. 

Electronic supplementary information (ESI) available: Recorded DSC curves, plots of eqn (1) (log $\delta$ versus 1000/$T_a$), tables with statistical and kinetic parameters, and experimental procedures. See DOI: 10.1039/c7ra08764k
mass of pristine fullerene C₆₀ or its derivative (Chart 1) and were dried in vacuum in 40 °C.

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 oxidation is detected. In non-isothermal DSC method the temperature is a linear function of time, thus, a temperature of start of oxidation (Tₑ, in °C) can be easily determined instead of time.

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 Tₑ increases, see Fig. 2. A similar increase can be observed when conjugates C₆₀-[I–IV] are added to HDPE: the values of Tₑ 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, Tₑ is shifted to higher temperatures and a magnitude of such shift is non-linearly proportional to concentration of the additive.

In our previous publications, we interpreted the shape of DSC curves of thermal effect of lipids and hydrocarbons oxidation and we proved that Tₑ parameter corresponds to constant degree of conversion (start of oxidation). Therefore,
that at temperatures below the isokinetic temperature, the activation energy (at concentration 0.065% w/w, whereas for Fig. 3 (log
with 0.5% BHT at temp. 100, 150 and 200
observed stabilizing e
containing 0.5% of BHT as a typical antioxidant widely used in
ethylene sample contains any of the four
fold decrease in comparison with pure HDPE). When poly-
rm the inhibitory properties of studied
C60 and its derivatives, as can be seen in Table 1 (log
C60-(I
25 kJ mol
the gas constant (8.314 J mol
Agreement with 127
values of activation energy of HDPE oxidation vary with the
pair of kinetic parameters
E
a is observed at concentrations 0.25% and 1%. Addition of pristine fullerene C60 to HDPE causes the growth of E_a with maximum at
Compounds C60-III and C60-IV exhibit maximal value of activation energy (134 ± 6 and 140 ± 3 kJ mol
respectively) at concentration 0.065% w/w, whereas for C60-I and C60-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 C60 and its derivatives C60-(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 C60 causes a decrease of k's within the whole range of concentrations (tenfold decrease in comparison with pure HDPE). When poly-
ethylene sample contains any of the four C60-(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/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
process with higher E_a is slower whereas at temp. above T_{iso} the process with higher E_a proceeds faster). For example, oxidation of polyethylene inhibited by 1% C60-III is described by E_a = 120 kJ mol
and Z = 1.2 × 10^{12} min
, giving the rate constants 1.85 × 10^{-5} min^{-1} at 100 °C and 0.066 min^{-1}
at 200 °C. If 1% C60-IV is used, the kinetic parameters E_a = 148 kJ mol
and Z = 3.7 × 10^{15} min^{-1} allow to calculate k_{100°C} = 8.33 × 10^{-15} min^{-1} and k_{200°C} = 0.193 min^{-1}. Thus, at 100 °C C60-IV is more active than C60-III whereas at 200 °C the derivative C60-III is more active than C60-IV. For this particular pair of kinetic parameters T_{iso} = ΔE_a/(8.334 × Δln Z) = 145 °C and indeed, rate constants presented in Table 1 for 150 °C are almost the same for C60-III and for C60-IV. Such inversions of the

\[ \log E_a = -2.19R(d \log Z/dT) \]  
\[ \log Z = \log(E_a/R) - b - 2.315 \]

where: R – the gas constant (8.314 J mol
°C), 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 ± 7 kJ mol
and Z = 1.11 × 10^{14} min
obtained for non-inhibited process (no additives) are in good agreement with 127 ± 6 kJ mol
and 7.15 × 10^{13} min
measured earlier\textsuperscript{a} as well as with other literature values.\textsuperscript{b,c} The values of activation energy of HDPE oxidation vary with the concentration of the added derivatives. Addition of pristine fullerene C60 to HDPE causes the growth of E_a with maximum at 0.5% w/w. Compounds C60-III and C60-IV exhibit maximal value of activation energy (134 ± 6 and 140 ± 3 kJ mol
respectively) at concentration 0.065% w/w, whereas for C60-I and C60-IV the maximal E_a is observed at concentrations 0.25% and 1%.

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>( E_a^c ) [kJ mol(^{-1})]</th>
<th>log k (min(^{-1})) at 150 °C</th>
<th>log k (min(^{-1})) at 150 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure HDPE</td>
<td>129 ± 7</td>
<td>14.04</td>
<td>-1.83</td>
</tr>
<tr>
<td>Fulleren derivative C60-I</td>
<td>0.065</td>
<td>127 ± 5</td>
<td>13.85</td>
</tr>
<tr>
<td>0.125</td>
<td>136 ± 8</td>
<td>14.66</td>
<td>-2.13</td>
</tr>
<tr>
<td>0.250</td>
<td>142 ± 8</td>
<td>15.04</td>
<td>-2.45</td>
</tr>
<tr>
<td>0.500</td>
<td>161 ± 8</td>
<td>17.06</td>
<td>-2.88</td>
</tr>
<tr>
<td>1.000</td>
<td>156 ± 7</td>
<td>16.33</td>
<td>-2.97</td>
</tr>
<tr>
<td>Fulleren derivative C60-II</td>
<td>0.065</td>
<td>141 ± 5</td>
<td>15.08</td>
</tr>
<tr>
<td>0.125</td>
<td>142 ± 8</td>
<td>15.04</td>
<td>-2.46</td>
</tr>
<tr>
<td>0.250</td>
<td>154 ± 4</td>
<td>16.13</td>
<td>-2.84</td>
</tr>
<tr>
<td>0.500</td>
<td>143 ± 4</td>
<td>14.79</td>
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</tr>
<tr>
<td>1.000</td>
<td>142 ± 7</td>
<td>14.65</td>
<td>-2.94</td>
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<tr>
<td>Fulleren derivative C60-III</td>
<td>0.065</td>
<td>134 ± 6</td>
<td>14.35</td>
</tr>
<tr>
<td>0.125</td>
<td>131 ± 4</td>
<td>13.83</td>
<td>-2.32</td>
</tr>
<tr>
<td>0.250</td>
<td>124 ± 5</td>
<td>12.99</td>
<td>-2.37</td>
</tr>
<tr>
<td>0.500</td>
<td>124 ± 3</td>
<td>12.81</td>
<td>-2.49</td>
</tr>
<tr>
<td>1.000</td>
<td>126 ± 3</td>
<td>12.95</td>
<td>-2.59</td>
</tr>
<tr>
<td>Fulleren derivative C60-IV</td>
<td>0.065</td>
<td>140 ± 3</td>
<td>14.77</td>
</tr>
<tr>
<td>0.125</td>
<td>132 ± 3</td>
<td>13.66</td>
<td>-2.64</td>
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<tr>
<td>0.250</td>
<td>128 ± 7</td>
<td>13.09</td>
<td>-2.74</td>
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<tr>
<td>0.500</td>
<td>130 ± 7</td>
<td>14.12</td>
<td>-2.87</td>
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<tr>
<td>1.000</td>
<td>120 ± 5</td>
<td>12.07</td>
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<tr>
<td>Fulleren derivative C60-IV</td>
<td>0.065</td>
<td>129 ± 5</td>
<td>13.89</td>
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<td>133 ± 5</td>
<td>14.27</td>
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<td>0.250</td>
<td>140 ± 3</td>
<td>15.03</td>
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<td>0.500</td>
<td>142 ± 8</td>
<td>15.09</td>
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<tr>
<td>1.000</td>
<td>148 ± 4</td>
<td>15.57</td>
<td>-2.64</td>
</tr>
</tbody>
</table>

\( \text{a Full data including statistic and kinetic parameters are given in ESI.}\)\( \text{b Concentration in % w/w.}\)\( \text{c Errors of the activation energy } E_a \text{ were calculated from the standard deviations of slopes calculated for confidence level 90%.}\)}
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 $T_{\text{iso}}$ while Fig. 3B presents the results calculated above $T_{\text{iso}}$. 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 $\alpha$-o-dimethylenophenol moiety, whereas the phenol residues in C$_{60}$-IV contain non-hindered hydroxyl groups. The Bond Dissociation Enthalpies (BDE) for O–H bond strength are the main reason responsible for increase of 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) suggesting rather weak reactivity of fullerene toward peroxyl radicals: rate constant of reaction of C$_{60}$ with cumylperoxyl radicals, $(3.1 \pm 1.1) \times 10^{-2} \text{ M}^{-1} \text{s}^{-1}$, is extremely slow compared to rate constant $(2.0 \pm 0.8) \times 10^{10} \text{ M}^{-1} \text{s}^{-1}$ for reaction with cumyl radicals. 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 ($k_{\text{inh}}$) and chain propagation ($k_{\text{p}}$). Depending on the $k_{\text{p}}$ for propagation of lipid or hydrocarbon, the same molecule can behave as a good antioxidant in hydrocarbon ($k_{\text{inh}}/k_{\text{p}} > 1000$) but with no antioxidant activity (no induction period will be observed) in unsaturated hydrocarbon ($k_{\text{inh}}/k_{\text{p}} \ll 1000$).

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 alkoxyl, alkyl, hydroxyl radicals as well as singlet oxygen formed during high temperature decomposition of peroxides (including non-Russel type reaction of tetroxides).

### 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

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1 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.
derivatives exhibit better antioxidant activity than C_{60} or phenols used alone, thus, increased efficacy of C_{60}–phenol conjugates is a result of a synergy between phenolic residues (reacting with peroxyl radicals by H-atom transfer) and C_{60} moiety (a “radical sponge” responsible for scavenging non-peroxyl 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**