

# Organotellurium Compounds as Stabilizers for Polymeric Materials

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## SYNOPSIS

The thermal stability of a series of organotellurium compounds was determined by thermogravimetric analysis and the stabilizing capacity of the most heat-resistant compounds assessed in natural rubber, polyethylene, and polypropylene by measurement of the oxidative induction time (OIT). The most active compounds, bis[4-(dimethylamino)phenyl]telluride (**5**) and bis[2,6-dimethyl-4-(dimethylamino)phenyl]telluride (**10**) stabilized natural rubber considerably at the 1% level and even more so at the 2% level. A similar stabilizing effect of compound **5** was found in polyethylene and polypropylene at the 0.1% level. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

A polymeric material may be degraded in several ways: However, the major differences between different aging processes are often related to the nature of the initiation step of a free-radical chain reaction, in which molecular oxygen is one of the reactants. This process is often referred to as autoxidation.<sup>1</sup> For example, polyethylene is degraded 10<sup>5</sup> times more rapidly in an oxygen atmosphere than in nitrogen at 260°C.<sup>2</sup> The autoxidation of simple low molecular-weight compounds is relatively well understood, but the oxidation of polymers is more complex.<sup>3</sup> The free-radical chain reaction is initiated by thermal, photochemical, or mechanical strain or by decomposition of peroxides or other impurities incorporated into the polymer during processing. The rate of oxidation of polymers is usually very low at ambient temperature, but the reactions cause a deterioration in physical properties. As the oxidation proceeds, the molecular weight is changed due to crosslinking or scission processes. This affects the stiffness, creep resistance, and brittleness of the material. Furthermore, oxidized polymers show

poorer mechanical strength and insulation capacity than do unoxidized polymers. Thus, the oxidative aging of polymeric materials is generally considered to be a deleterious process and considerable efforts have been devoted to inhibiting or suppressing it. Various kinds of stabilizers<sup>4</sup> such as chain-breaking antioxidants, UV-absorbers, peroxide decomposers, and metal complexing agents have been tested over the years.

We have studied the antioxidative properties of various organotellurium compounds for some time. As judged by the results obtained with several model systems, organic tellurium compounds can act both as peroxide decomposers<sup>5-7</sup> and as chain-breaking antioxidants.<sup>8,9</sup> This has induced us to investigate the stabilizing capacity of organotellurium compounds in polymeric systems.

The antioxidative properties of organotellurium compounds in mineral oils, fats, lubricants, and greases were claimed in some early patents.<sup>10</sup> However, to the best of our knowledge, the only recent account on the use of organotelluriums for polymer stabilization is a report by McWhinnie et al. on PVC stabilization.<sup>11</sup> In the present investigation, the thermal stabilities of a series of organotellurium compounds were assessed by thermogravimetric analysis (TGA). The most heat-resistant compounds were then mixed into natural rubber (NR), polyeth-

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ylene (PE), and polypropylene (PP) and the stabilizing capacities of the additives were determined by measurement of the oxidative induction time (OIT).

## EXPERIMENTAL

The thermogravimetric analyses were carried out under nitrogen, using a Perkin-Elmer TGA-2 analyzer. The samples were heated at a rate of 10°C/min. The temperatures shown in Table I correspond to the loss of 5% of the initial sample weight. OIT experiments were performed using a Perkin-Elmer DSC-4 apparatus. Five milligram samples were enclosed in Al capsules and four small holes were bored through the lids to facilitate oxygen transport during the analysis. Melting points given for new compounds are uncorrected. <sup>1</sup>H-NMR spectra, obtained at 250 MHz, were recorded for CDCl<sub>3</sub> solutions containing tetramethylsilane as the internal standard. Tetrahydrofuran was freshly distilled from potassium. Elemental analyses were performed by Analytical Laboratories, Engelskirchen, Germany. Natural rubber (NR) was a gift from Skega AB, Ersmark, Sweden. Polyethylene (PE) powder was obtained from Neste OY and polypropylene (PP) granules from ICI. NR were prepared by melt blending unstabilized NR (30 g) with the appropriate amount of stabilizer at 70–72°C for 10 min using a Plasti-Corder (Brabender OHG). Plaques of the blended materials were then produced under press (10 ton/cm<sup>2</sup>) at 70°C for 10 min between two films of cellulose. PE and PP samples were prepared similarly by melt blending at 165°C. The organotellurium compounds, **1**,<sup>12</sup> **2**,<sup>13</sup> **3**,<sup>7</sup> **4**,<sup>14</sup> **5**,<sup>15</sup> **6**,<sup>7</sup> **7**,<sup>16</sup> **8**,<sup>15</sup> and **9**<sup>15</sup> were prepared according to procedures described in the literature.

### Bis[2,6-dimethyl-4-(dimethylamino)phenyl]telluride (10)

A solution of bromine (5.75 g, 35.9 mmol) in acetic acid (6 mL) was added to a stirred solution of *N,N*,3,5-tetramethylaniline (5.35 g, 35.9 mmol) in acetic acid (20 mL) and the stirring was continued for 24 h. The reaction mixture was then treated with methylene chloride and neutralized with NaOH (2M aq). After separation of the organic phase, drying, and evaporation, the residue was recrystallized from MeOH/H<sub>2</sub>O to yield 6.7 g (82%) of 4-bromo-*N,N*,3,5-tetramethylaniline. <sup>1</sup>H-NMR (δ): 6.45 (s, 2H), 2.89 (s, 6H), 2.38 (s, 6H).

*Tert*-Butyllithium (10.3 mL 1.7M, 17.5 mmol) was added dropwise under argon to a stirred and

cooled (−78°C) solution of 4-bromo-*N,N*,3,5-tetramethylaniline (2.0 g, 8.76 mmol) in THF (30 mL). After 30 min, the cooling bath was removed and freshly crushed elemental tellurium (1.12 g, 8.8 mmol) was added in one lot. The stirring was then continued for 1 h and the reaction mixture poured into a separatory funnel containing CH<sub>2</sub>Cl<sub>2</sub> (30 mL), water (30 mL), and K<sub>3</sub>Fe(CN)<sub>6</sub> (2.9 g, 8.8 mmol). After vigorous shaking, the organic phase was washed with water and dried (MgSO<sub>4</sub>) and the solvent evaporated. Treatment with copper powder (5.0 g) in refluxing dioxane<sup>17</sup> afforded 1.32 g (71%) of the title compound, mp 161–163°C (EtOH). <sup>1</sup>H-NMR (δ): 6.45 (s, 2H), 2.9 (s, 6H), 2.39 (s, 6H).

ANAL: Calcd for C<sub>20</sub>H<sub>28</sub>N<sub>2</sub>Te: C, 56.65%; H, 6.66%. Found: C, 56.82%; H, 6.60%.

### Bis[4-(dimethylamino)-2,3,5,6-tetramethylphenyl]telluride (11)

4-Bromo-2,3,5,6-tetramethylaniline<sup>18</sup> (1.91 g, 8.37 mmol), formaldehyde (3.37 g 37% aq, 42 mmol), and formic acid (5 mL) were heated under reflux<sup>19</sup> for 16.5 h. After addition of water (25 mL), the reaction mixture was neutralized by addition of NaHCO<sub>3</sub> and the product was extracted into CH<sub>2</sub>Cl<sub>2</sub> (3 × 40 mL). Flash chromatography (hexanes) of the crude material afforded 1.87 g (87%) of 4-bromo-*N,N*,2,3,5,6-hexamethylaniline. By using the procedure for preparation of compound **10**, the title compound **11**, mp 187–190°C, was prepared in 77% yield from 4-bromo-*N,N*,2,3,5,6-hexamethylaniline. <sup>1</sup>H-NMR (δ): 2.85 (s, 12H), 2.45 (s, 12H), 2.25 (s, 12H).

ANAL: Calcd for C<sub>24</sub>H<sub>36</sub>N<sub>2</sub>Te: C, 60.03%; H, 7.56%. Found: C, 59.90%; H, 7.47%.

## RESULTS AND DISCUSSION

Qualitative and quantitative thermochemical studies of organotellurium compounds in the solid state are rare. From the few studies reported,<sup>20</sup> it can be concluded that diaryl tellurides as well as diaryl ditellurides tend to extrude elemental tellurium when heated. Thermogravimetric analyses of a series of organotellurium compounds were carried out under nitrogen and the results are presented in Table I. The temperatures given correspond to the point at which 5% of the initial weight has been lost.

It is evident from our previous studies<sup>5–9</sup> on model systems that diaryl tellurides carrying electron-donating substituents are the most efficient per-

**Table I** Stability of Organotellurium Compounds as Determined by TGA Analysis

Compound No.	Formula	Decomposition Temperature <sup>a</sup> (°C)
1		240
2		160
3		220
4		210
5		220
6		240
7		120
8		160
9		140
10		240
11		230

<sup>a</sup> 5% of the initial sample weight has been lost.

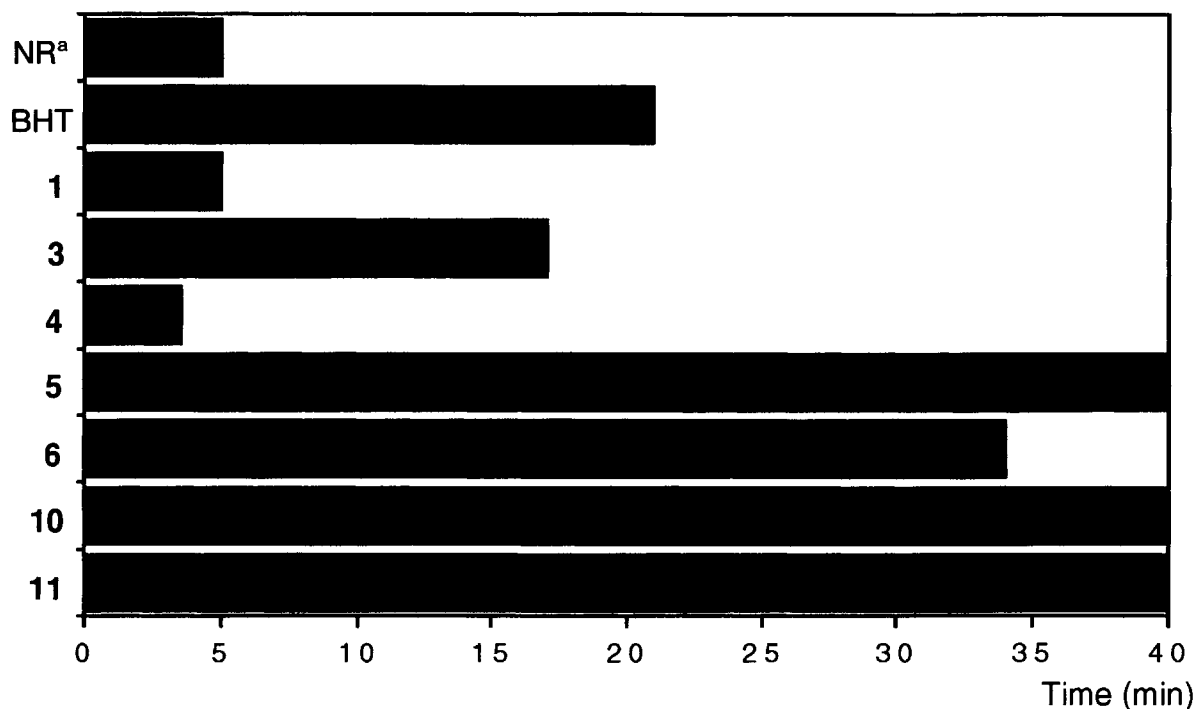
oxide decomposers and chain-breaking antioxidants. However, the simple 4,4'-dihydroxy-, 4,4'-di(phenylamino)-, and 4,4'-diamino-substituted diphenyl tellurides **2**, **8**, and **9** were decomposed at or below 160°C (Table I). Poor thermal stability was also observed for diphenyl ditelluride (**7**). Bis[4-(dimethylamino)phenyl]telluride (**5**), on the other hand, was stable up to 220°C under nitrogen. It was also found that the introduction of methyl groups generally increased the thermal stability of diphenyl tellurides. Thus, compounds **3**, **4**, **6**, **10**, and **11**, containing hydroxyl, methoxyl, or dimethylamino groups, were all stable at least up to 210°C (Table I).

The extent of the degradation in a polymer can be studied through measurement of the oxidative induction time (OIT). OIT is related to the amount and kind of antioxidant added to the polymer and the test temperature used. The OIT is measured with a differential scanning calorimeter used in its isothermal mode. In our experimental setup, a capsule containing the polymer sample was rapidly heated (200°C/min) to the experimental temperature in an atmosphere of oxygen and the time from baseline stabilization to the onset of rapid exothermic oxidation of the tested material was recorded. This technique of aging assessment addresses the chemical properties rather than the mechanical properties that are commonly determined for the life assessment of polymers.

The most heat-resistant diphenyl tellurides (2% w/w) were mechanically mixed into NR and OIT measurements were carried out on plaques at 176°C (Table II). 2,6-Di(*t*-butyl)-4-methylphenol (BHT), a commonly used processing antioxidant, was included as a reference compound. Telluride **1** (OIT = 5 min), lacking electron-donating hydroxyl or amine substituents and the phenolic compound **4** (OIT = 3 min), did not improve the heat resistance of NR (OIT = 5 min for the unstabilized reference sample). The phenolic compound **3** (OIT = 17 min) was almost as efficient as was BHT as a stabilizer, and compound **6** (OIT = 34 min) was more efficient than was the reference antioxidant. However, compounds **5**, **10**, and **11** were much more efficient stabilizers of NR than was BHT and attempts to measure OIT at 176°C, and even at 190°C, only resulted in straight lines with an infinitesimal slope (OIT ≥ 40 min). However, at the 1% level, the OIT at 176°C for compounds **5**, **10**, and **11** were measurable (21, 24, and 4 min, respectively). At lower concentrations (0.1 and 0.5% w/w), compound **5** showed only a very poor stabilizing capacity.

Compound **5** was also melt-blended into PE and PP. At a concentration of 0.1% w/w, the OIT at 210°C was 23 min for PE (untreated sample 7 min). The OITs at 190°C for the stabilized and unstabilized samples of PP were 29 and 3 min, respectively.

Concerning the mechanism of the stabilizing action of diphenyl tellurides in polymeric materials, we can only speculate: The efficient diphenyl telluride stabilizer **5** has a very low oxidation potential (0.50 V vs. Ag/AgCl [Ref. 13]). Thus, it may be capable of reducing radicals formed, thereby delaying the onset of the free-radical chain reaction which leads to rapid exothermic degradation of the material.

**Table II** OIT at 176°C for NR, Stabilized with 2% of One of the Organotellurium Compounds or BHT

<sup>a</sup> Unstabilized natural rubber.

Since its discovery, tellurium has found several commercial applications as an additive element.<sup>21</sup> It is added to steel and copper for improving machinability. It has also been used in rubber as a vulcanizing agent, in glass and ceramics as a coloring agent, and for the formulation of semiconducting compounds. Organotellurium compounds, prepared from elemental tellurium or simple inorganic derivatives thereof (e.g., TeCl<sub>4</sub>), could therefore not be expected to be prohibitively expensive for large-scale use.

Concerning toxicity, elemental tellurium has not been found to be very hazardous.<sup>22</sup> Although organotellurium compounds are generally considered less toxic than their organoselenium counterparts, there is certainly a need for more knowledge about the toxicity of these compounds.

## CONCLUSIONS

We have demonstrated, for the first time, that organotellurium antioxidants can be used for the stabilization of NR, PE, and PP. In view of their high stabilizing capacity, high thermal stability, high molecular weight, and, hence, low volatility, we presume that organotellurium compounds should be

useful for the stabilization of a variety of polymeric materials.

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