

Stabilization of PACREL[®] by Organotellurium Compound

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ABSTRACT: The addition of 0.17–0.50% of bis[4-(dimethylamino)phenyl]telluride to the thermoplastic elastomer PACREL[®] significantly improved tensile strength and elongation at break in unaged and oven-aged samples. Chemiluminescence measurements showed that the organotellurium compound considerably prolonged the induction period of thermooxidation of the material and drastically reduced the total luminescence intensity of unaged and aged samples. These results indicate that the improved mechanical properties of diaryl telluride stabilized PACREL[®] can be attributed to the antioxidative (peroxide decomposing, chain breaking) properties of the stabilizer. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 449–556, 1998

Key words: PACREL[®]; improved mechanical properties; chemiluminescence measurements; organotellurium compound; antioxidant

INTRODUCTION

The thermo- and photooxidative aging of polymers causes a deterioration in their physical and mechanical properties. As the oxidation proceeds, the molecular weight is changed due to crosslinking or scission processes. Discoloration of the material is frequently observed. Poorer mechanical strength often results and properties such as stiffness, creep resistance, and brittleness are affected. The deleterious consequences of oxidative aging can be inhibited, or at least relieved, by the addition of chain-breaking antioxidants, UV absorbers, metal-complexing agents, and peroxide decomposers.¹

Organotellurium compounds have occasionally been described in the patent literature.² Aromatic,

hydroxyaromatic, and alkyl tellurides were early claimed to act as oxidation and corrosion inhibitors for mineral and lubricating oils. Diaryl and alkyl aryl tellurides were also used in electrophotographic compositions, photographic emulsions, and photothermographic photosensitive materials. More recently, diaryl tellurides were found to stabilize immunoassay compositions. Some time ago, we started a more systematic investigation of the antioxidative properties of organotellurium compounds. Diaryl tellurides, which are a particularly stable class of organotellurium compounds, were found to be readily oxidized by hydrogen peroxide and organic hydroperoxides from the divalent to the tetravalent state.^{3,4} Thus, the compounds act as peroxide decomposers. Due to their ready one electron oxidation, diaryl tellurides were also found to act as chain-breaking donating antioxidants.^{5,6} This antioxidative action also results in oxidation of the chalcogen atom to the stable tetravalent state. Because many mild reducing agents are known to reduce tetravalent tellurium to the divalent state, it

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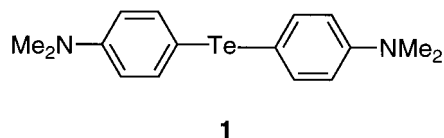
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Table I Mechanical Properties of PACREL® 206 Blends

Compound 1 (%)	0	0	0	0.3	0.3	0.3
Aging time (weeks)	0	4	4	0	4	4
Aging temp. (°C)	23	23	40	23	23	40
Hardness (°/shore A)	74	75	76	74	74	76
Modulus (MPa)						
MD	11 ± 0.5	11 ± 0.3	12 ± 0.5	9 ± 0.3	9 ± 0.3	10 ± 0.2
TD	8 ± 0.4	8 ± 0.2	8 ± 0.5	8 ± 1	8 ± 1	9 ± 0.3
Tensile strength (MPa)						
MD	4 ± 0.1	4 ± 0.1	4 ± 0.1	4 ± 0.1	4 ± 0.1	4 ± 0.1
TD	3 ± 0.1	3 ± 0.1	3 ± 0.2	4 ± 0.2	4 ± 0.1	4 ± 0.1
Elongation at break (%)						
MD	139 ± 7	147 ± 6	108 ± 8	185 ± 6	185 ± 4	181 ± 9
TD	221 ± 23	222 ± 24	222 ± 31	259 ± 19	258 ± 5	246 ± 12

MD, machine direction; TD, transverse direction.

should be possible to use organotelluriums as catalytic antioxidants. This kind of action was recently demonstrated in a two-phase model system for lipid peroxidation using a thiol as a stoichiometric reducing agent.⁷ In summary, organotellurium compounds seem to act as multifunctional catalytic antioxidants in model systems. It occurred to us that these capacities, if expressed in a polymeric matrix, would be very useful for stabilization. Although inorganic tellurium compounds (elemental tellurium and its oxides and/or halides; tellurium diethyldithiocarbamate)⁸ have been utilized for the stabilization of rubbers, silicon elastomers, and polypropylene (PP) and dialkyltellurium maleates have been used as thermal and UV stabilizers for polyvinyl chloride,⁹ organotellurium compounds have not been sufficiently examined for their ability to enhance the aging resistance of polymeric materials. With the intention to develop new tellurium-based stabilizers for polymeric materials, we recently investigated the thermal stability and stabilizing capacity in natural rubber, polyethylene, and PP of a series of diaryl tellurides.¹⁰ As judged by thermogravimetric analysis and oxidative induction time (OIT) measurements, bis[4-(dimethylamino)phenyl]telluride (**1**) was thermally stable up to 220°C and considerably stabilized natural rubber at the 1–2% level. This result prompted us to study the effects of organotelluriums in other polymeric materials. In this article we report on the stabilization of PACREL®, a thermoplastic elastomer,¹¹ with the organotellurium compound **1**. In contrast to the previous study, an aging assessment was used that focuses on changes in the mechanical rather than the chemical properties of the material.



EXPERIMENTAL

Materials

Reactor made PACREL® 632, PACREL® 631, and PACREL® 206 were obtained from Optatech Corp. A compounded sample of PACREL® 632 containing oil and conventional stabilizers was also obtained from the manufacturer. Bis[4-(dimethylamino)phenyl]telluride (**1**) was prepared according to a literature procedure.¹²

Preparation of Test Samples

Samples of PACREL® containing compound **1** were prepared by the following procedures. The samples used for recording the mechanical properties in Table I were prepared on a 2-kg scale by first preparing a master batch (5%) of the stabilization compound on a Brabender twin-screw extruder. The temperature profile was 170, 180, and 180°C and the screw speed 70 rpm. This master batch was then mixed with more PACREL® and twice homogenized in the twin-screw extruder.

The stabilization packages in the samples in Tables II and III were prepared in the same way as a master batch by using a Werner & Pfleiderer ZSK 25 M940D twin-screw extruder. The temperature profile was 190, 190, 190, 190, 190, and

Table II Mechanical Properties of PACREL® 632 Blends

	0.2	0.2	0.2	0.2	0.2	0	0	0	0
Compound 1 (%)	0.2	0.2	0.2	0.2	0.2	0	0	0	0
Aging time (weeks)	0	10	4	10	10	0	4	4	10
Aging temp. (°C)	23	23	80	80	80	23	80	80	80
Hardness (°/shore A)	95	95	—	94	94	92	—	—	94
Modulus (MPa)									
MD	171 ± 15	150 ± 22	185 ± 25	125 ± 20	125 ± 20	176 ± 43	177 ± 14	125 ± 8	145 ± 15
TD	112 ± 21	81 ± 11	98 ± 4	76 ± 9	76 ± 9	82 ± 14	109 ± 7	84 ± 11	74 ± 10
Modulus 100% (MPa)									
MD	9 ± 0.2	10 ± 0.3	11 ± 0.6	11 ± 0.5	11 ± 0.5	9 ± 0.2	10 ± 0.3	9 ± 0.2	0 ± 0
TD	6 ± 0.1	7 ± 0.1	7 ± 0.2	7 ± 0.1	7 ± 0.1	6 ± 0.3	7 ± 0.2	6 ± 0.2	7 ± 0.1
Tensile strength (MPa)									
MD	10 ± 0.1	10 ± 0.3	11 ± 0.6	11 ± 0.4	11 ± 0.4	9 ± 0.2	10 ± 0.3	10 ± 0.1	5 ± 1.1
TD	8 ± 0.1	8 ± 0.1	9 ± 0.3	9 ± 0.2	9 ± 0.2	7 ± 0.3	8 ± 0.4	7 ± 0.4	7 ± 1.7
Elongation at break (%)									
MD	187 ± 21	167 ± 15	132 ± 10	137 ± 13	137 ± 13	179 ± 20	127 ± 9	173 ± 17	14 ± 5
TD	281 ± 19	245 ± 5	228 ± 20	251 ± 13	251 ± 13	266 ± 7	203 ± 28	236 ± 37	164 ± 84

MD, machine direction; TD, transverse direction.

190°C and the speed was 150 rpm. The output was 4.5–5 kg/h.

The materials were then injection molded in an Engel ES 200/40 injection molding machine. The melt temperature was 180°C, and the dimensions of the test plate were 80 × 80 × 2 mm.

The samples used for recording the mechanical properties in Table IV were prepared on a 40-g scale by melt blending of the components in a Brabender mixer at 180°C for 5.5 min. Plaques (3 mm) of the blended materials were then produced under press at 170°C (1.5 min).

Tensile and Hardness Tests

Tensile properties were measured on Instron 4204 (Table I; 1-kN load cell, 500 mm/min) and a Zwick 1465 (1-kN load cell) testing machines. Elongation was recorded with an extensometer (Tables II, III). The standard specimens were punched out in both the machine direction and transverse direction from the injection molded plates. Modulus and elasticity was measured at a speed of 1 mm/min, then 500 mm/min (Tables II, III). Hardness was measured according to ISO 48 (shore A). Tensile properties in Table IV were measured on an Instron 5566 instrument.

Chemiluminescence

For induction time measurements, a CLD 100 chemiluminescence detector from Tohuko was used as described by Forsström and coworkers.¹³ At the onset of the experiment, the temperature was increased from 25 to 150°C at an average heating rate of 3°C/min and then kept at this temperature throughout the experiment. For total luminescence intensity (TLI) measurements, an Alnor thermoluminescence dosimeter reader, which was described by Mattson and coworkers,¹⁴ was used. Its main advantage is extremely rapid heating. The samples were lifted into a preheated stream of nitrogen, and TLI was recorded during 3 min at 150°C.

Dynamic Mechanical Thermal Analysis (DMTA)

Dynamic mechanical properties were investigated with a DMTA Mark II from Polymer Laboratories working in the bending mode (single cantilever). Temperature scans were from –70 to +150°C at a heating rate of 5°C/min. The frequency was 1 Hz and the strain amplitude 16 μm.

¹H-NMR Measurements

For the assessment of the thermal stability of compound 1, 5-mg samples were heated in NMR

Table III Mechanical Properties of PACREL® 632 Blends Compounded with Oil and Conventional Antioxidants

Compound 1 (%)	0	0	0	0
Aging time (weeks)	0	10	4	10
Aging temp. (°C)	23	23	80	80
Hardness (°/shore A)	85	86	—	82
Modulus (MPa)				
MD	69 ± 13	46 ± 3	65 ± 10	41 ± 5
TD	34 ± 3	30 ± 3	35 ± 4	33 ± 3
Modulus 100% (MPa)				
MD	7 ± 0.3	8 ± 0.1	8 ± 0.3	8 ± 0.3
TD	5 ± 0.1	5 ± 0.2	5 ± 0.1	6 ± 0.2
Tensile strength (MPa)				
MD	8 ± 0.4	8 ± 0.1	8 ± 0.3	8 ± 0.3
TD	7 ± 0.6	7 ± 0.3	7 ± 0.5	8 ± 0.5
Elongation at break (%)				
MD	133 ± 5	130 ± 1	109 ± 4	110 ± 6
TD	188 ± 36	216 ± 9	196 ± 21	198 ± 20

MD, machine directions; TD, transverse direction.

tubes under the conditions (time and temperature) indicated. The residue was then dissolved in deuterated chloroform (1 mL) and the ¹H-NMR spectrum recorded at 300 MHz.

RESULTS

Mechanical Properties

PACREL® thermoplastic elastomers are composed of a continuous PP phase and a lightly crosslinked (vulcanized) polybutylacrylate phase.¹¹ The two-phase structures are prepared by a special solid-state polymerization described recently.^{15–17} The

mechanical properties of reactor made PACREL® 206, reactor made PACREL® 206 stabilized with 0.3% compound 1 (Table I), reactor made PACREL® 632, reactor made PACREL® 632 stabilized with 0.2% compound 1 (Table II), and PACREL® 632 compounded with oil and conventional antioxidants (sterically hindered amines and phenols as heat and light stabilizers; (Table III) as determined immediately after preparation and after aging (4 or 8 weeks) in an oven at various temperatures (23, 40, and 80°C) are shown in Tables I–III. For PACREL® 206 (Table I), the hardness of the material was unaffected by the antioxidant whereas the tensile modulus in the flow but not in the transverse direc-

Table IV Mechanical Properties of PACREL® 632 Blends

Compound 1 (%)	Aging Temp. (°C)	Aging Time (weeks)	Tensile Strength (MPa)	Elongation at Break (%)
0	23	0	3.8 ± 0.2	79 ± 22
0	70	4	2.6 ± 0.5	25 ± 9
0	70	9	2.3 ± 0.3	21 ± 4
0.17	23	0	7.1 ± 0.5	124
0.17	70	4	6.4 ± 0.8	84 ± 34
0.17	70	9	7.4 ± 0.6	130 ± 45
0.30	23	0	6.2 ± 0.1	197 ± 8
0.30	70	4	6.6 ± 0.5	168 ± 29
0.30	70	9	6.5 ± 0.7	146 ± 30
0.50	23	0	7.1 ± 0.7	200 ± 68
0.50	70	4	7.4 ± 0.3	167 ± 25
0.50	70	9	7.6 ± 0.5	184 ± 25

tion was slightly lowered. The tensile strength in the transverse direction was improved by 25% by the addition of compound **1** whereas the elongation at break increased by about 11–17%. Notably, the improvements in the mechanical properties were seen before aging of the material. For PACREL® 632 (Table II), the amount of antioxidant was lowered (0.2%) and the material aged for a longer time at higher temperature. Again, the hardness of the material was not affected by aging and the presence of compound **1**. Also, no trends could be seen in the values recorded for the tensile modulus. The tensile strength of diaryl telluride stabilized material did not change appreciably upon 10-week aging at 80°C. For unstabilized material in the flow direction, a 50% reduction in strength was observed after similar treatment. The most dramatic differences between stabilized and unstabilized samples were seen in the values for elongation at break. In the flow direction after 10 weeks at 80°C, the values for unstabilized reactor made PACREL® were only 10% of those recorded for telluride stabilized material. Table III presents the mechanical properties of PACREL® 632 stabilized by commercial antioxidants. Because the material is also compounded with oil (see hardness and tensile modulus), no direct comparison with the values reported in Tables I and II can be made. However, it should be clear that the organotellurium compound increases the resistance to aging of PACREL® at least as much as conventional antioxidants.

The mechanical properties of PACREL® 631 were evaluated in another series of experiments. In this approach, the mechanical measurements were complemented with chemiluminescence measurements (*vide infra*). Samples containing 0, 0.17, 0.30, and 0.50% diaryl telluride **1** were aged in an oven at 70°C for 0, 4, and 9 weeks, respectively. The results are presented in Table IV. As noted above, the organotellurium compound caused a significant improvement in the mechanical properties. Thus, in the presence of 0.17% of the stabilizer, the tensile strength and elongation at break were almost unchanged after 9 weeks at 70°C. The corresponding values for the unstabilized material were reduced by 40 and 75%, respectively. Interestingly, the improved mechanical properties were observed in the unaged samples.

Chemiluminescence

Due to the development of single-photon counting equipment, the chemiluminescence technique has

recently become useful for the study of degradation of polymeric materials.¹⁸ Chemiluminescence measures the low level of light emission that accompanies oxidation of organic materials. Chemiluminescence time traces recorded in oxygen at 150°C for PACREL® 631 stabilized with 0.17–0.5% diaryltelluride **1** showed significantly longer induction times (60–70 min) than for the unstabilized material (30 min). This shows that the antioxidative properties of the organotellurium compound previously observed in organic solvents can also be expressed in a polymeric matrix. Heating O₂-free samples rapidly decomposes all peroxidic groups and gives a TLI that is proportional to the peroxide content of the material. Figure 1 shows the TLI as a function of aging time (at 70°C) for samples of PACREL® 631 stabilized with 0, 0.17, 0.30, and 0.50% diaryl telluride **1**. In all three stabilized samples, the initially low TLI is only slightly increased (2–5 times) by aging. As expected, the increase is inversely related to the amount of stabilizer present. In the unstabilized sample, the initial TLI is approximately 10 times higher than for stabilized material and it increases by a factor of 13 during aging.

Dynamic Mechanical Properties

Figure 2 shows the $\tan \delta$ versus temperature for unstabilized PACREL® 631 and for PACREL® 631 containing 0.3% organotellurium compound **1**. Clearly, the addition of the stabilizer suppresses the $\tan \delta$ of the polybutylacrylate phase.

Stabilizer Stability

The thermal stability of diaryl telluride **1** was previously studied by thermogravimetric analysis. As judged from these measurements, 5% of the initial sample weight was lost at 220°C in an atmosphere of nitrogen. To assess the chemical stability of compound **1** under more userlike conditions, samples of the material were heated neat in NMR tubes in air at various temperatures and times. The cooled samples were then diluted with deuterated chloroform and their ¹H-NMR spectra recorded. As shown in Figure 3, only very slight decomposition of the material occurred by heating at 180°C for 10 min. After heating at 215°C, approximately 80% of the starting material remained after 15 min. So far, the decomposition products have not been further analyzed. However, none of the telluroxide corresponding to telluride **1** is formed under these conditions. It

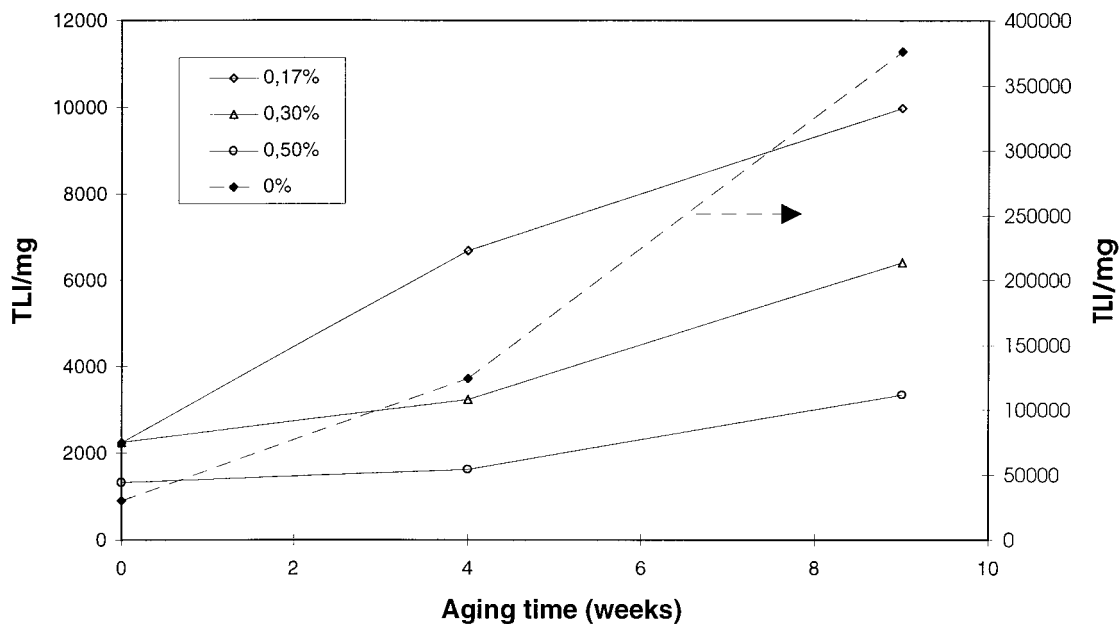


Figure 1 TLI as a function of aging time at 70°C for samples of PACREL® 631 stabilized with 0, 0.17, 0.30, and 0.50% diaryl telluride **1**. The right luminescence scale is for unstabilized material only.

should be pointed out that the purity of the stabilizer is critical for the extent of decomposition. Thus, slightly impure samples of compound **1** showed significant decomposition (20%) when heated at 180°C for 10 min.

DISCUSSION

Studies of the mechanical properties of the thermoplastic elastomer PACREL® (especially after aging at 80°C) clearly indicated that the material requires a

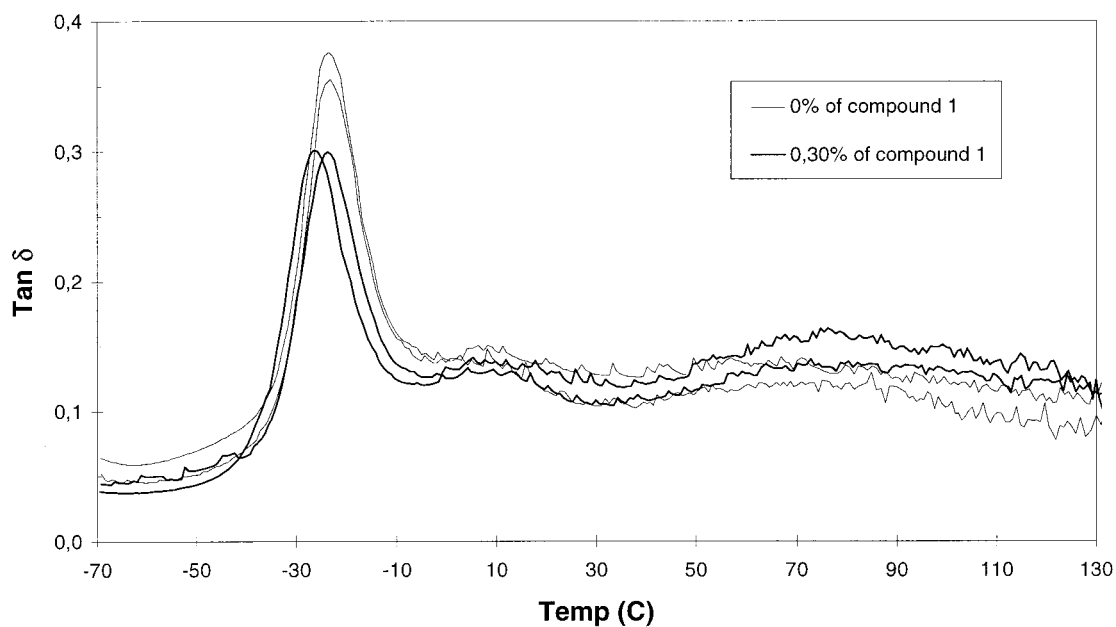


Figure 2 Tan δ as a function of temperature for PACREL® 631 stabilized with 0 and 0.30% diaryl telluride **1**.

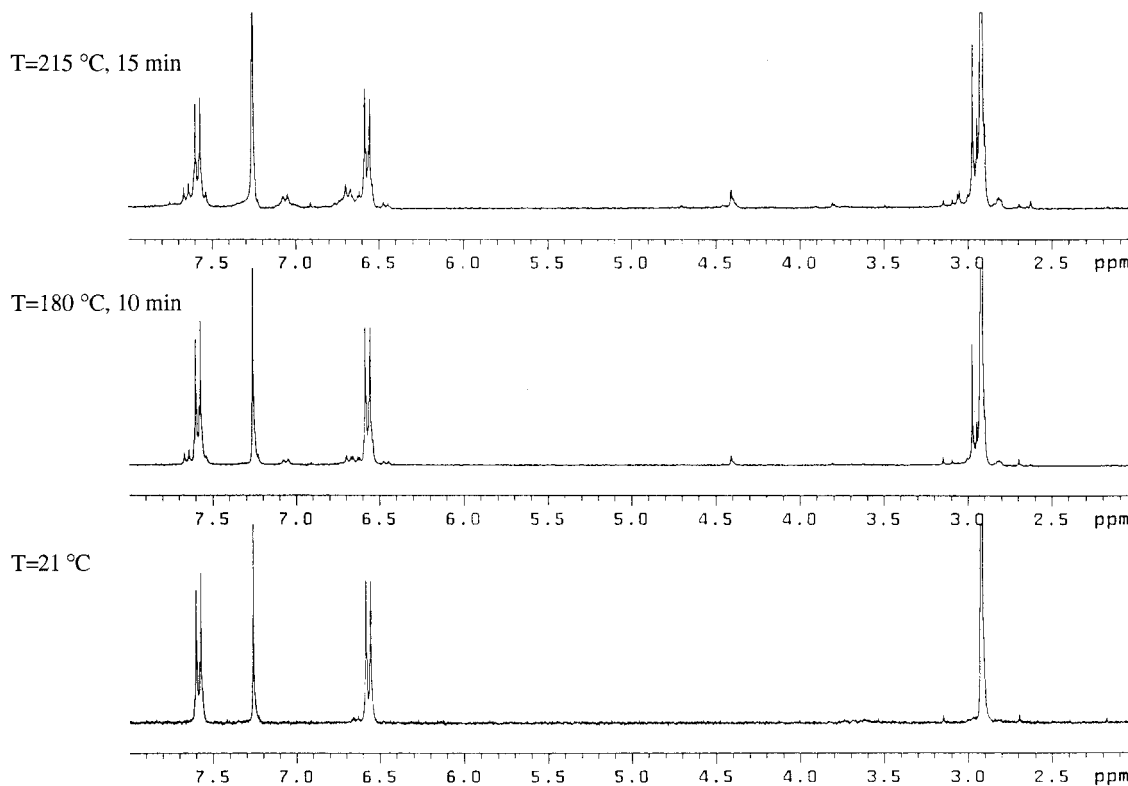


Figure 3 Thermal stability of compound **1** as determined by $^1\text{H-NMR}$ spectroscopy. NMR spectra were recorded in deuteriochloroform after heating at the temperatures and times indicated.

stabilizer to resist thermooxidative degradation. As compared with unstabilized material, the organotellurium compound **1** (0.17–0.50%) considerably improved tensile strength and elongation at break of unaged, as well as aged, samples. Chemiluminescence studies indicated that the organotellurium compound considerably prolonged the induction period of oxygen stimulated oxidation of the material and drastically reduced the TLI of unaged and aged samples as compared with the unstabilized control. These results clearly show that the improved properties of telluride stabilized PACREL® can be attributed to the antioxidative properties of the stabilizer. Considering its complex mode of antioxidative action, it is not obvious why the organotellurium compound causes an improvement of the mechanical properties of unaged samples. The thermal lability of the stabilizer may indicate that it at least partially falls apart during processing at elevated temperature, thus initiating radical processes that could increase crosslinking of the acrylate phase. In support of this idea, the DMTA measurements showed decreasing damping peaks associated with the butylacrylate phase. However, the hardness and tensile modulus are essentially unaf-

ected by admixing of the diaryl telluride and swelling experiments gave no indication of increased crosslinking. Improved mechanical properties of unaged samples may also result if the stabilizer promotes compatibility and interfacial adhesion in the PP-polybutylacrylate blend. However, because the compatibilization reactions rely on a reaction between a nucleophile in the PP with an electrophile in the polybutylacrylate,¹¹ it is difficult to see how the very weak bis-nucleophile **1** could increase compatibility between the two phases. The known peroxide decomposing capacity of diaryl telluride **1** could possibly also explain the improved mechanical properties of unaged samples that contain it. Chemiluminescence measurements clearly indicate that diaryl telluride stabilized samples of PACREL® 631 contain far less peroxidic species than unstabilized material. Probably, diaryl telluride is partially oxidized to a telluroxide while contacted with the polymeric material during processing (processing antioxidant).

It is now well established that selenium is an essential trace element in humans. In contrast, surprisingly little is known of the occurrence and role of tellurium in biological systems. Several

studies have indicated that trace amounts of tellurium are present in body fluids such as blood and urine. Tellurium has been shown to cause neuromuscular defects in animals via induced demyelination of peripheral nerves.¹⁹ However, the element is not considered very toxic to animals and humans.²⁰ Although organotellurium compounds of the type investigated in this study are generally considered less toxic than their organoselenium counterparts, there is a need for more knowledge about the effects of these materials in animals, humans, and the environment.

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