Efficiency of Antioxidants in Thick-Walled Natural Rubber Samples Evaluated by Differential Scanning Calorimetry and Compression Stress–Relaxation

B. STENBERG and F. BJÖRK, *Department of Polymer Technology, The Royal Institute of Technology, S-100 44 Stockholm, Sweden*

Synopsis

The effect ot two antioxidants, IPPD and DENA, on the aging properties of TMTD-vulcanized natural rubber was studied by DSC. In the case of IPPD, the results were compared with mechanical measurements. The DSC measurements were carried out on specimens taken at different depths from cylindrical samples. The decrease in oxidative induction time was less pronounced for IPPD than for DENA at the edge of the samples. In the interior, the opposite behaviour was observed.

INTRODUCTION

Antioxidants are added to unsaturated rubbers in order to prolong the lifetime of rubber products. There is a comprehensive literature on this subject such as recent publications Refs. 1–4. The investigations reported generally relate to either the mechanism of oxidation, the oxidation process, the products of oxidation, or the mechanism of stabilization.

Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) have been used to determine the amounts and the efficiencies of different stabilisers.[5,6] Smith and Stephens[8] have used DSC to evaluate the effects of different antioxidants in unvulcanized rubbers.

An oxidative induction time (OIT) is usually defined as the time which elapses before an oxidative reaction starts, as illustrated in Figure 1. When the antioxidant is consumed, an exothermal reaction starts. Smith and Stephens[8] have shown that two exothermal reactions occur with unsaturated elastomers. The first exothermal reaction in the 180–200°C region was attributed to an oxidative crosslinking reaction, and the second in the 350–400°C region to polymer degradation or chain scission. They concluded, in agreement with Bauman and Maron,[9] that both low-temperature and high-temperature processes were involved.

When the effectiveness of antioxidants in rubbers is studied, the DSC apparatus is usually operated isothermally (isothermal method) at a preselected temperature. This temperature is usually between 170 and 220 °C depending on the polymer and antioxidant. A lowering of the test temperature prolongs the induction period, but makes it more difficult to define the induction time. The test is performed in oxygen, and it is essential that
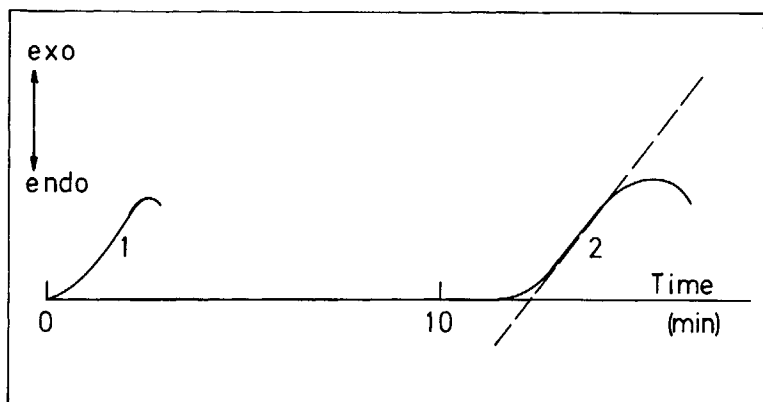
Fig. 1. DSC scan showing different oxidative induction times for rubber without (1) and with (2) antioxidant.

the measurements are made so that the heat evolved is exchanged with the sample holder. Goh[10] has used DSC to study the effectiveness of antioxidants and their effects on the activation energy of oxidation of unvulcanised natural rubber.

We now report an analysis by DSC of how the antioxidant concentrations vary with aging time at different depths thick-walled natural rubber samples. In the case of IPPD, the results of the OIT measurements are compared with results of mechanical measurements (compression relaxation).

EXPERIMENTAL

The compositions of the materials used are shown in Table I. ISAF is intermediate superabrasion furnace black and serves as a reinforcing filler. ZnO and stearic acid form the activator system. TMTD (tetramethyl thiuramdisulfide) is a vulcanization agent and gives compounds with excellent aging resistance. During the vulcanization, TMTD forms mono- and disulfidic crosslinks and also dithiocarbamate which is claimed to be a powerful antioxidant.[11] The abbreviations IPPD and DENA stand for N-isopropyl-N'-phenyl-p-phenylene diamine and N,N-diethyl-p-nitrosoaniline, respec-

TABLE I
Composition of Materials Used[a]

	A	B	C
Natural rubber	100	100	100
ISAF (N 220)	50	50	50
ZnO	5	5	5
Stearic acid	1	1	1
TMTD	8	8	8
IPPD	0	2	0
DENA	0	0	2

[a] Vulcanization time = 20 min; vulcanization temperature = 174°C.

tively, both of which are antioxidants. Cain et al[12] have described the effect and use of the network-bound antioxidant DENA. All samples were made by the Swedish rubber factory, Skega AB, S-934 02 Ersmark, Sweden, whose cooperation is gratefully acknolwedged.

The three different material compositions that were studied are shown in Table I. Material A had no antioxidant, material B contained IPPD, and Material C DENA. The samples were cylinder-shaped with a diameter equal to the height of 25 mm. The samples were aged in air at 100°C in an oven. Samples were taken out of the oven after different aging times for OIT analysis. To map the state of antioxidant efficiency at different depths in the rubber cylinders, specimens with a volume of approximately 1 mm³ for OIT measurements were taken out at the center of the sample and at distances 7 and 12 mm from the centre along the radius (in Figs. 2 and 3 these different depths are assigned 0, 7, and 12 mm from the center). The specimens taken 12 mm form the center were thus taken at the edge of the sample.

The oxidative induction time (OIT) was recorded with a Perkin-Elmer DSC-I apparatus. Specimens weighing about 15 mg were encapsulated in DSC capsules. The upper side of each capsule was perforated with 25–30 holes to facilitate oxygen transport to the rubber. The specimen holder of the DSC apparatus was heated to 200°C, and the oxygen flux through the specimen holder was adjusted to 20 mL/min. The OIT was measured from the moment when the encapsulaed specimen was placed in the specimen holder.

A calibration curve of OIT vs. antioxidant concentration was obtained from DSC measurements on a series of specimens with different known
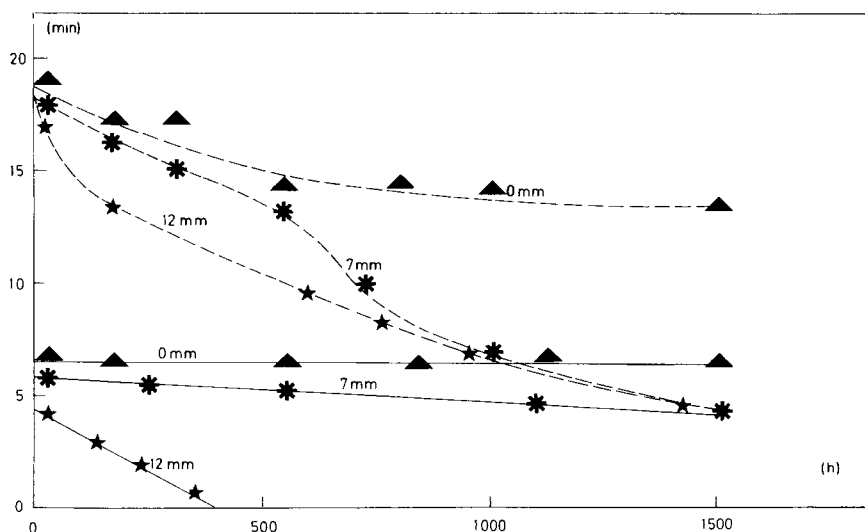

Fig. 2. OIT-curves for material A (—) and material B (- - -) measured at indicated depths. 0 mm = center of the sample; 12 mm = the edge of the sample.
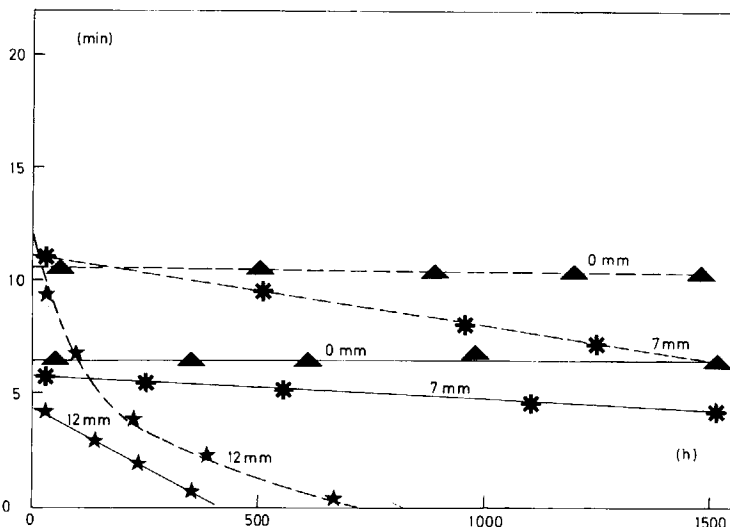
Fig. 3. OIT-curves for material A (—) and material C(- - -) measure at the indicated depths. 0 mm = center of the sample; 12 mm = the edge of the sample.

concentration of IPPD prepared by refluxing natural rubber specimens in toluene containing known concentrations of antioxidant for 24 h. All toluene-soluble material was removed by extraction before the immersion in IPPD. To avoid any influence of oxygen, all extraction, immersion, and drying was done in a nitrogen atmosphere. It was assumed that the IPPD would be uniformly distributed between rubber and toluene. This was checked by weighing the specimens. The weight gain after immersion was in good agreement with the calculated IPPD uptake.

The compression relaxation measurements were performed on materials A and B at 20% compression and 100°C with a relaxometer described earlier.[13] The samples were allowed to come to temperature equilibrium for 0.5 h before measurements were started.

RESULTS

Figure 2 shows curves of oxidative induction time for materials A and B as a function of aging time at different depths in the sample, and in Figure 3 corresponding results are presented for materials A and C. Figure 4 presents a comparison of compression relaxation data for materials A and B. The relaxation was calculated according to the expression

$$R(t) = 100 \cdot F(t)/F(t_n) \qquad (1)$$

where $F(t)$ is the stress measured at time t and $F(t_n)$ is the stress measured at a reference time t_n, which was chosen to be 10 min after compression of the sample. Before compression of the sample, temperature equlibrium was established for 30 min. Through this procedure, the physical relaxation was minimized.

The calibration curve obtained for OIT against concentration of IPPD (Fig. 5) was not linear but was slightly curved towards the antioxidant
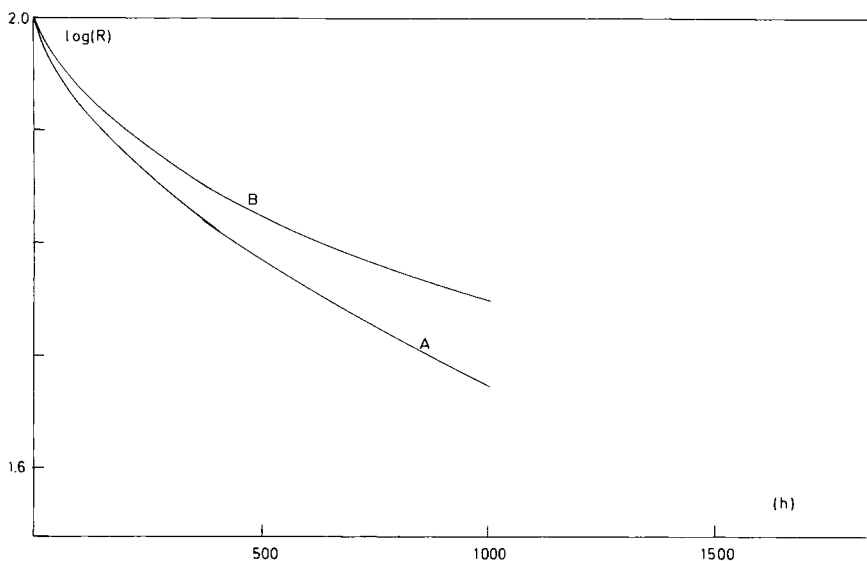
Fig. 4. Compression relaxation curves at 100°C as a function of aging time, materials A and B.

concentration. This can be explained as being due to the simulataneous occurrence of two competing reactions, evaporation, and consumption of antioxidant.

DISCUSSION

Initially we tried to use a more technical vulcanization system based on sulfur and CBS (*N*-cyclohexyl-2-benzothiazole sulfenamide) but, since residues from the vulcanization system appeared as a vulcanization exotherm which overlapped the exotherm from the oxidative reaction, it was almost impossible to obtain reliable OIT data for S/CBS vulcanizates. The TMTD system was chosen for our investigations, since this problem did not arise in this case.

The decrease in OIT with aging time and the positive effect of the antioxidants are obvious in Figures 2–4. As can be expected, the decrease in
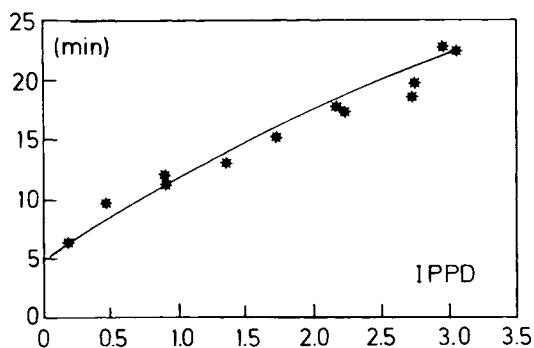

Fig. 5. Curve showing how the OIT depends on the concentration of IPPD in the rubber.

OIT is most rapid at the outer oxygen-exposed parts of the samples. In the inner parts of the samples the OIT decreases slowly with increasing aging time. The long-term effect of IPPD in material B is clearly seen (Fig. 2), and the positive effect of the network-bound antioxidant DENA (Fig. 3) is obvious. After 1500 h of aging material B with IPPD still gave an OIT of 5 min at a distance of 12 mm from the center of the sample (Fig. 2). For material C with DENA the OIT at the same place in the cyclinders is almost zero after at about 700 h (Fig. 3). At a distance of 7 mm from the center of the sample, the OIT for material C is longer than for material B at this depth if the aging time exceeds 700 h. Diffusion of IPPD from the interior of the samples prolongs the OIT at distances of 12 mm from the center. No such effect can be found with DENA. At a distance of 7 mm from the center of the cylinders OIT in material B is shortened because IPPD difuses out of the material. At this point in cylinders of material C, the OIT decreases very slowly, probably because diffusion of oxygen into the material is the only process shortening the OIT after an initial period of aging. The same effect is found in the center of the cylinders.

Activation energies were determined from DSC measurements performed at five different temperatures. The values obtained are:

Material A 120 kJ/mol

Material B 148 kJ/mol

Material C 166 kJ/mol

These values are probably mean values of activation energies for evaporation and consumption of antioxidants. These values are in good agreement with values reported earlier.[4,5]

In Figure 4, material B shows a slower relaxation rate than material A, and this positive effect is ascribed to IPPD. A comparison shows that the OIT data in Figure 2 and the mechanical data in Figure 4 support each other.

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