

Stress-Relaxation of Natural Rubber under Compression—Dependence on Oxygen Concentration

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Synopsis

The compression-relaxation was studied for unfilled TMTD-vulcanized natural rubber cylinders (height = diameter = 20 mm). The samples have been treated prior to compression in different oxygen media from an inert medium to pure oxygen at 2.0 MPa. Activation energies were calculated from compression-relaxation measurements made at different temperatures, and from these results conclusions were drawn concerning the diffusion control of the relaxation.

INTRODUCTION

Most stress-relaxation studies on rubber materials have been made on thin-walled samples, so that the relaxation rate was not diffusion-controlled. The oxygen content in the atmosphere has been found to strongly effect the stress-relaxation for thin-walled rubber specimens.¹ For thick-walled rubber specimens it has been found that oxygen under increased pressure significantly influences the permanent set.²

We now report a study of how the oxygen concentration in thick-walled unfilled TMTD-vulcanized natural rubber samples influences the rate of the stress-relaxation under compression at elevated temperatures. Samples have been treated prior to compression in different oxygen media from an inert medium to pure oxygen at 2.0 MPa.

MATERIALS

Cylindrical natural rubber samples (height = diameter = 20 mm), having the composition NR (natural rubber) 100, ZnO 5, TMTD (tetramethylthiuram disulphide) 4, stearic acid 1 phr (parts per hundred rubber), were used.

EXPERIMENTAL

Vulcanized samples were treated according to one of the following procedures:

1. Storage at 70°C for 72 h in air at 0.1 MPa.
2. Storage at 70°C for 72 h in oxygen at 2.0 MPa.
3. Storage at 70°C for 168 h in oxygen at 2.0 MPa.
4. Treatment according to procedure 3 followed by storage at room temperature in air at 0.1 MPa for 144 h.
5. Storage at 70°C for 72 h in nitrogen at 1.5 MPa.
6. Storage at 55°C for 78 h in vacuum (10^{-9} – 10^{-11} MPa).

The treatment at elevated pressures (procedures 2-5) were carried out in an oxygen bomb at Sieverts Kabelverk AB, Sundbyberg, Sweden, whose cooperation we gratefully acknowledge.

Immediately after a treatment, relaxation measurements were started at 20% compression at 100°C in the relaxometer shown in Figure 1. The compression is set by the upper nut, which is fixed in position by a lock nut. The lower nut is then tightened against the plate to hold the compression at a constant value. The force is registered by a load cell, which is connected to a measuring bridge. A thermostated oven holds the temperature at the desired level. The samples were allowed to come to temperature equilibrium for 0.5 h before measurements were taken.

The relaxation values were calculated according to the formula:

$$R = f(t)/f(0) \times 100$$

where $f(t)$ = force at time t , $f(0)$ = force at time $t = 0.5$ hour after compression of the sample. A normalizing time of 0.5 h was selected in order to minimize the physical relaxation in the initial stage of the relaxation.

Samples pretreated according to 1 and 2 were used to determine the energy of activation for the thermooxidative degradation. The relaxation was measured at three different temperatures (90°C, 105°C, and 120°C) at 20% compression over a period of 5 h. The normalization time was set to 5 min and 30 min. Five minutes was chosen so that the incorporated oxygen should not be consumed before the measurement started. With a normalization time of 30 min most of the incorporated oxygen was supposed to be consumed. The log R was plotted

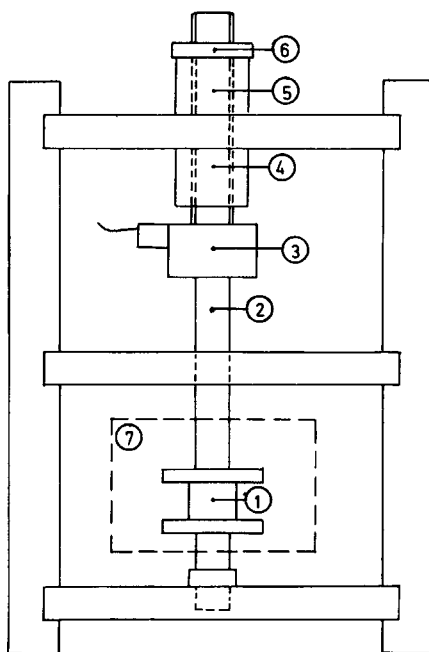


Fig. 1. Relaxometer: (1) sample; (2) compression rod; (3) load cell; (4) lower nut; (5) upper nut; (6) lock nut; (7) oven.

TABLE I
Crosslink Densities

	mol/cm ³
Initial crosslink density	1.6×10^{-4}
Crosslink density after procedures	
1	1.6×10^{-4}
2	1.5×10^{-4}
3	1.2×10^{-4}
5	1.6×10^{-4}

against linear time, so that a rate constant could be calculated assuming that first-order kinetics were applicable.

In all relaxometer measurements, the surfaces of the samples were lubricated with silicone grease to reduce the shear stresses at the end surfaces.

Swelling was measured before and after the treatments according to procedures 1–6. The effective network chain density was calculated from these swelling measurements using the Flory–Rehner equation. The samples were swollen in *n*-heptane for 72 h at 30°C after the soluble fraction had been removed by extraction in *n*-heptane for 24 h. The value used for the solvent–polymer interaction parameter was 0.46 according to Kraus.³ The results are presented in Table I.

RESULTS AND DISCUSSION

The relaxation curves at 100°C resulting from treatments according to procedures 1–6 are shown in Figure 2. The relaxation rate after treatment in oxygen at 2 MPa (procedure 2) is higher than the relaxation rate after treatment in air at 0.1 MPa (procedure 1). As the crosslink density is almost the same, it is reasonable to explain this increase as being due to the difference in oxygen treatment, which raises the oxygen concentration in the sample. After still longer times in oxygen (procedure 3) the relaxation rate is further increased, but a part of this increase, as can be seen in Table I, can be explained as being due to a decrease in crosslink density. The difference between curves 3 and 4 is a measure of how much oxygen has left the sample during 144 h storage. The oxygen forced into the rubber sample under high pressure evidently diffuses outwards from the rubber rather slowly, an appreciable amount of oxygen being left in the

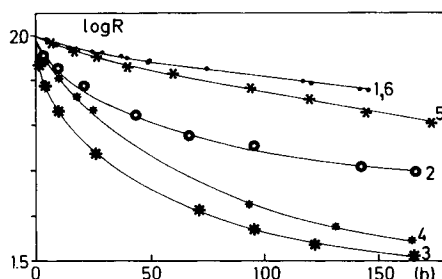


Fig. 2. Logarithmic relaxation at 100°C plotted against linear time for treatments according to procedures 1–6.

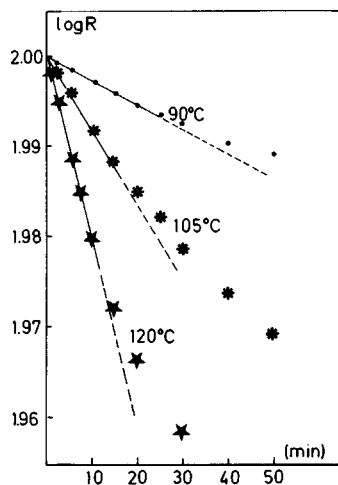


Fig. 3. Logarithmic relaxation curves against linear time at different temperatures. Normalization time 5 min. Samples treated according to procedure 2.

sample after storage in room temperature for 144 h. Procedure 5 was undertaken in order to replace incorporated oxygen by nitrogen. Only a small effect was obtained. Instead of using a static pressure we plan to repeat this by allowing nitrogen to flow through a sheet of rubber. Our efforts to pump out oxygen under vacuum from the rubber sample evidently had no effect, since procedures 6 and 1 gave identical relaxation curves. Oxygen is obviously not removed by evacuation and this can be due to the fact that oxygen is not dissolved in the rubber, but is rather firmly bonded to the rubber network.⁴ The relaxation curves in Figure 2 level off and for long aging times low relaxation rates results.

Figures 3 and 4 show the relaxation curves at different temperatures with a normalization time (t_0) equal to 5 min. The curves corresponding to a normalization time of 30 min have the same appearance as those in Figure 3 and 4, but they are not shown here. From the initial straight lines, the slopes (k) were calculated. The values obtained are plotted in Figure 5 as $\log k$ against reciprocal

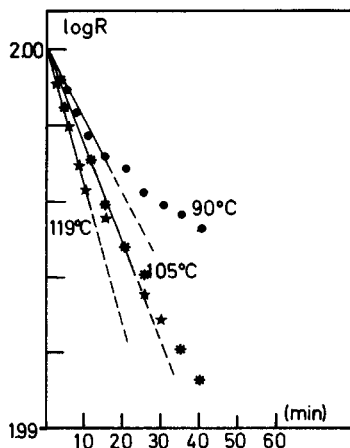


Fig. 4. Logarithmic relaxation against linear time at different temperatures. Normalization time 5 min. Samples treated according to procedure 1.

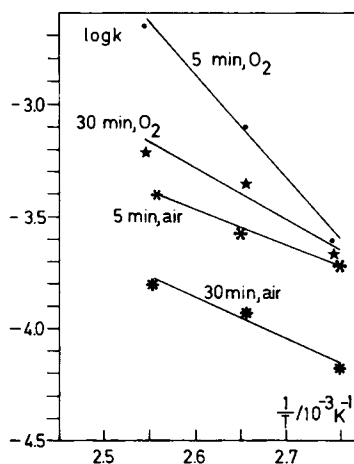


Fig. 5. Arrhenius plot of logarithmic relaxation rate against reciprocal temperature.

TABLE II
Energy of Activation for Procedures 1 and 2 at Normalization Times

Procedure	Normalization time (min)	ΔH (kJ/mol)
1 (0.1 MPa air)	5	29
1 (0.1 MPa air)	30	34
2 (2.0 MPa O ₂)	5	85
2 (2.0 MPa O ₂)	30	40

temperature (T). The calculated activation energies obtained from the normalization times of 5 and 30 min are presented in Table II. Two levels for the activation energy were found. The lower level of about 30 kJ/mol is almost identical with the activation energy for diffusion of oxygen in rubber.⁵ The activation energy of 85 kJ/mol probably represents a mixture between thermooxidative degradation and diffusion. After 30 min the relaxation is completely diffusion-controlled, presumably because the oxygen concentration in the sample has sunk so that the thermooxidative degradative process is again governed by oxygen diffusing from the surrounding atmosphere into the rubber.

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