

# Transient Length Dilation vs. Transient Increase in Permeability of Natural Rubber Films

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## SYNOPSIS

Air dissolved under pressure in a film, made from natural rubber, causes its slight dilation. Sudden decompression of this film leads to its large transient dilation that afterwards vanishes within less than a minute ( $\tau \approx 20$  s). Such transient expansion is apparently caused by internal stresses due to oversaturation. This behavior is analogous to the previously reported transient increase in the permeability to gases of the suddenly decompressed polymeric membranes. A clear correlation between results derived from the dilation and the permeability measurements seems to be evident.

## INTRODUCTION

It was recently shown that the permeability of membranes may increase momentarily by a large factor without loss in selectivity when they are suddenly decompressed during gas permeation.<sup>1</sup> This behavior has been attributed to transient changes in membrane morphology, induced by the internal pressure of the excess of the dissolved gases. A microcavitation on a nearly molecular level has been postulated to explain the mechanism of such transient changes.<sup>1b</sup> Accordingly, one could expect that changes in the permeability will be accompanied by a transient increase in the volume of the depressurized membranes. Measurements of dilation or contraction in one or two dimensions may provide an estimate of volume changes in isotropic materials.

Instrumentation that enables performance with good precision of such transient measurements in membranes has been described by Pope et al.<sup>2</sup> It was decided, therefore, to find out if a correlation between transient changes in permeability and membrane dimensions may, indeed, be observed.

## EXPERIMENTAL

Schematic representation of a dilatometer system used for measurements of changes in the length of

membranes, induced by a sudden decrease or increase in pressure, is shown in Figure 1. Eight-mil-thick, 12-cm-long, and 1.5-cm-wide strips of the natural rubber (NR) latex type samples were cut from films supplied by Tagum Inc., Israel, that were also used for permeation experiments. All measurements were conducted at 35°C. Membrane strips were suspended in the Jerguson gage and pressurized in air in 100 psi increments from 0 to 541 psia. Each pressurization increment was completed in approximately 15 s. The kinetics of dilation were determined by noting the change in length every few seconds after the pressurization step was completed. Dilation isotherms were also determined, in addition to these kinetic measurements, after the investigated samples were equilibrated at pressures ranging from 100 to 541 psia.

Pressurized samples were depressurized within 15.6–16.2 s from 541 psia to atmospheric pressure. Such a pressurization–depressurization procedure was repeated twice for each sample. The temperature changes during the pressurization and the depressurization steps were also measured. Two Omega “Cement-On” chromel–alumel thermocouples were suspended in the center of the Jerguson gage (care was taken not to touch its metal sides). One thermocouple was uncoated and measured the temperature of the air. The second was coated with the natural rubber (by successive immersion in its solution) to a thickness approaching that of the actual NR sample. The final thickness of the natural rubber coating formed on the thermocouple was approxi-

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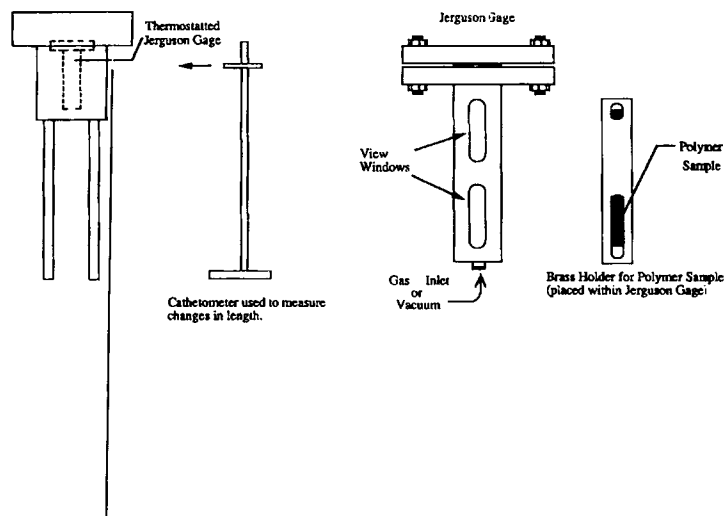


Figure 1 Schematic of volume dilation equipment.

mately 6 mil. The cell was evacuated, pressurized, and depressurized in a manner very similar to that used in the actual dilation experiments. The thermocouples provided almost instantaneous temperature readings at any point during the pressurization and depressurization procedures.

## RESULTS AND DISCUSSION

Elongation of 0.06–0.08% per 100 atm of the NR films, caused by pressurization, may be attributed to expansion of its volume by the additional gas dissolved in it under the applied pressure (cf. data summarized in Table I). However, the initial much larger increase of 0.4–0.6%/100 atm that relaxes eventually to the equilibrium value seems to be due to thermal expansion caused by transient increase in the temperature of the sample after the compression of the gas in the cell. Indeed, relaxation times, of the two perturbations calculated from measurements of temperature and dilation after pressurization, are nearly identical.<sup>†</sup>

A more complex behavior is, however, observed during the depressurization step. Analysis of the dilation curves obtained for such experiments indicates that an additional factor or factors must be

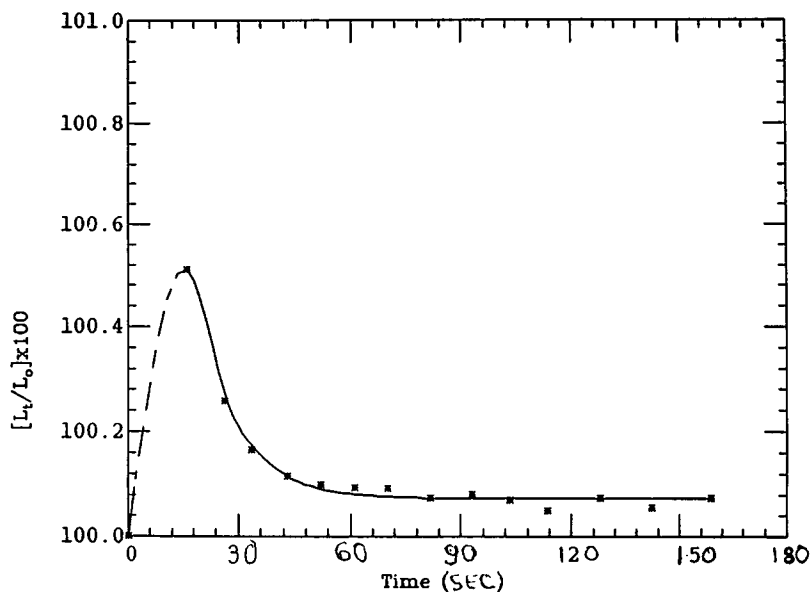
considered to account for the behavior of the NR samples under such conditions.

Inspection of Figure 4 reveals that dimensional changes that follow sudden release of pressure acting on the film cannot be described as a simple reversal of those that take place during the pressurization step. Only the initial contraction, which takes place immediately after pressure drop, seems to be a reversal of the initial expansion after pressure jump and may be attributed to the cooling of the NR sample. Subsequent expansion is much larger than expected for the return of the sample to its equilibrium value. Thus, after ca. 40 s, when the temperature of the sample nearly returns to equilibrium (cf. Fig.

Table I Dilation Isotherm at 35°C for NR at 14.7–560 psia

Pressure (psi)	$(L_p/L_0) \times 100$			
	Sample 1		Sample 2	
	Cycle 1	Cycle 2	Cycle 1	Cycle 2
0.0	0.0	0.0	0.0	0.0
100.9	—	—	100.0998	—
105.0	100.0699	100.082	—	100.0583
207.1	—	—	100.1386	100.1358
211.1	—	100.1397	—	—
300.7	100.207	100.1922	100.2134	100.185
386.3	—	100.239	—	100.2272
407.3	100.275	—	100.2965	—
507.1	100.3108	—	—	—
541.2	—	100.3318	100.371	100.298

<sup>†</sup> The solid line in Figure 2 that fits very well the experimental points was computed for  $\tau_L = 11.27$  s as the relaxation time of the perturbation of sample's length during its pressurization from 200 to 300 psia. Similar calculations, based on data collected for the perturbation of its temperature during such pressurization step, yield  $\tau_T = 12.03$  s (cf. Fig. 3) for the 200–300 psia range and  $\tau_T = 10.91$  s for the 100–200 psia range.



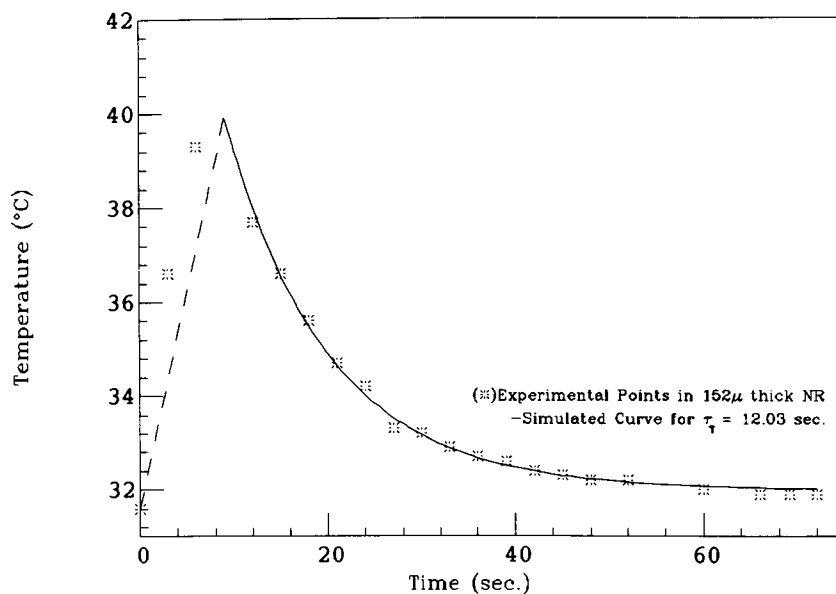
**Figure 2** Changes in sample length during pressurization from 200 to 300 psia. Natural rubber (NR) in air at 35°C.

5), its elongation reaches a maximum of 1–2% in excess of its equilibrium value. Afterwards the expanded sample starts to relax back to its initial length. Obviously, an additional expansion is superimposed on dimensional changes due to temperature fluctuations and it is followed by the final relaxation process or processes.

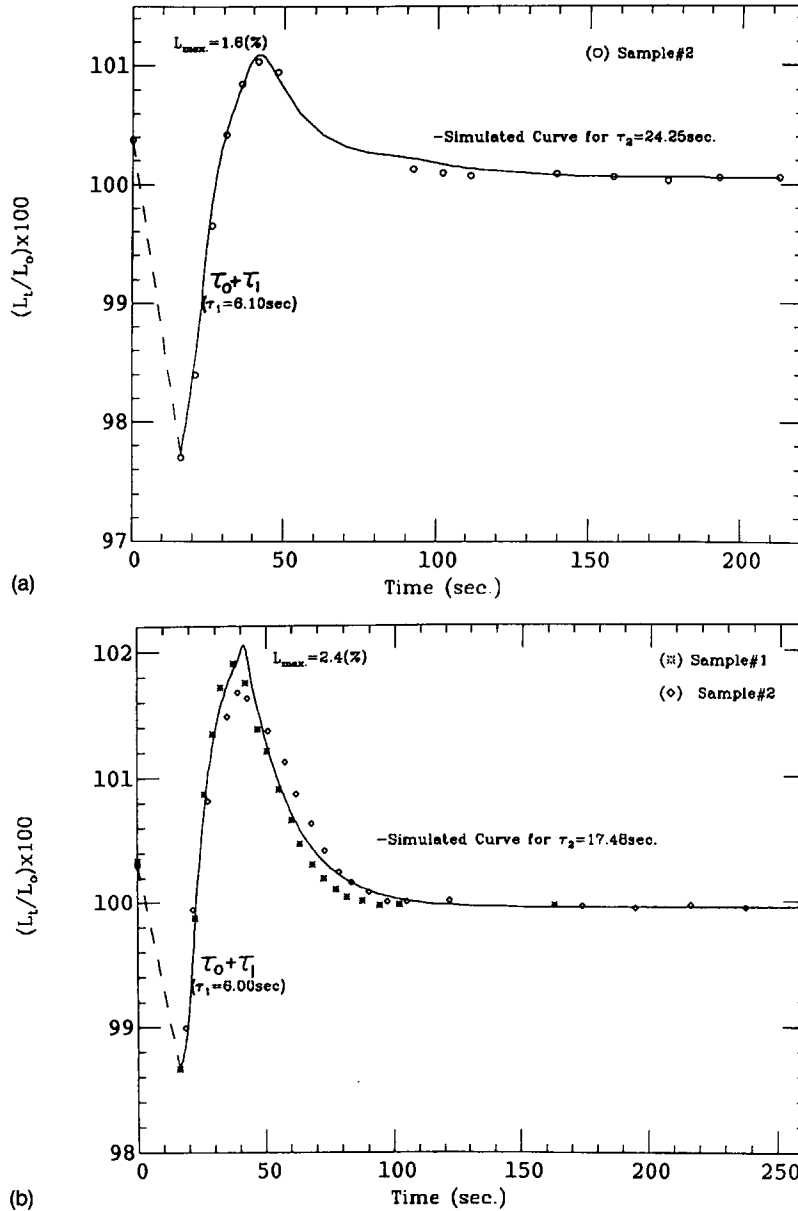
The continuous line in Figure 4 was computed by a computer simulation procedure that used the SAS

Synlin and Nlin routines for a best fit between the experimental and the calculated points. It was assumed that the initial contraction caused by cooling of the sample during the fast decompression is followed by an expansion step that involves a superposition of two distinct processes:

- (1) Return of the sample to its initial dimensions that follows its warming back to its initial



**Figure 3** Temperature changes in a 150  $\mu$ m thick NR coating during compression from 200 to 300 psia.



**Figure 4** Changes in sample length during decompression from 541 to 14.7 psia. Natural rubber (NR) in air at 35°C: (a) cycle #1; (b) cycle #2.

temperature. The relaxation time of this process,  $\tau_0$ , was assumed to be the same as that of its *thermal relaxation*,  $\tau_{Td} = 16.7$  s, calculated from temperature measurements shown in Figure 5.

- (2) Additional *transient expansion* to a length of  $L_{max} = L_0 + \Delta L_{max}$ , characterized by the relaxation time  $\tau_1$ .

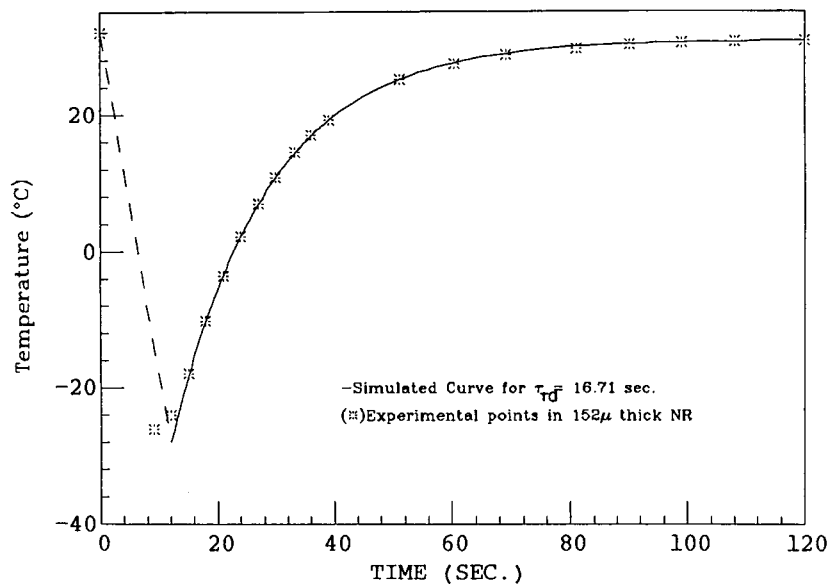
It was further assumed that the *final* relaxation step (characterized by  $\tau_2$ ) begins when the transient expansion ends.

Simulation of the first relaxation process was started at the beginning of the rise in temperature

and of the second relaxation process (additional transient expansion) at the end of pressure drop. The final relaxation step (contraction from  $L_{max}$  to  $L_0$ ) was started somewhat arbitrarily when the experimental results showed a maximum of elongation. Accordingly, the following equation was used for the computer simulation procedures:

$$L_t = L_{min} + (L_0 - L_{min}) \times (1 - \exp(16 - t)/16.7) + \Psi$$

$$\Psi = \Delta L_{max} \times \{ f_1 [1 - \exp(20 - t)/\tau_1] - f_2 [1 - \exp(42 - t)/\tau_2] \}$$



**Figure 5** Temperature changes in a 150  $\mu\text{m}$  thick NR coating during decompression from 541 to 14.7 psia.

where  $L_0$  and  $L_{\min}$  denote the length of the sample before compression and of its experimentally measured minimum length after decompression, respectively. Value of  $f_1$  was taken as 0 and as 1, respectively, before and after 20 s from the start of the decompression. Values of  $f_2$  were taken as 0 and 1, respectively, before and after 42 s from the start of the decompression.

The results obtained in the first pressurization-depressurization cycle seemed to differ significantly from those of the second cycle and were treated separately. The following values of  $\tau_1$ ,  $\tau_2$ , and  $\Delta L_{\max}$  were found to give the best fits shown in Figure 4:  $\tau_1 = 6.10 \pm 0.49$  s;  $\tau_2 = 24.25 \pm 3.38$  s; and  $\Delta L_{\max} = 1.6\%$  for cycle #1; and  $\tau_1 = 6.00 \pm 0.47$  s;  $\tau_2 = 17.48 \pm 0.98$  s; and  $\Delta L_{\max} = 2.4\%$  for cycle #2.

Thus derived expansion behavior of the simulated contraction-expansion-contraction curves fits very well the experiment [cf. Fig. 4(a) and 4(b)] and essentially identical values of  $\tau_1$  were derived from experimental values obtained in cycles #1 and #2, respectively. Simulation of the *final* relaxation step, based on the assumption of a single relaxation mechanism, gave a less perfect fit. It is possible, therefore, that more than one relaxation contributes to this step. Indeed, it was found that as many as three relaxation mechanisms are involved in the stress relaxation of this material.<sup>‡</sup> An attempt to

<sup>‡</sup> An excellent fit of the experimental and the simulated stress relaxation results for these NR samples was obtained on the assumption that three simultaneous relaxations (13.2, 58.6, and  $15 \times 10^3$  s) are involved.

improve the fit of the simulated curves by introduction of additional adjustable parameters does not seem, however, to be justified in this case.

The observed transient expansion of the NR samples due to their sudden decompression have been expected by us on the basis of previous studies of their permeability. It is reasonable to assume that such an expansion may be induced by internal stresses caused by a gas, previously dissolved in the membrane under high pressure and now in excess. This observation seems to provide, therefore, supporting evidence for the claim that such internal stresses may lead to a transient microcavitation on a nearly molecular scale, which is apparently responsible for a large transient increase in gas permeation of the suddenly decompressed NR samples.<sup>1</sup>

Asymmetric temperature gradients that arise as result of sudden decompression of a membrane during a permeation experiment may facilitate such changes. The above phenomenon may be related to the nucleation step in the formation of *macroscopic* gas bubbles during decompression of certain elastomeric samples, which has been previously described in the literature.<sup>3</sup> However, our model does not require an initial presence in the material of small spherical voids.

Irregularly shaped voids may expand their volume without any change in surface area by becoming spherical. Such a transformation of the molecular size and shape voids is postulated to be involved in the process observed by us. In such a way, a fast release of the internal stresses generated by the su-

persaturation may be achieved without a considerable expenditure of energy. Hence, only free energy loss due to decrease in the cohesive energy and entropy of the system, caused by the required disentanglement and separation of polymeric chains, is involved.

Dimensional restrictions imposed on a sample in a permeability cell may perhaps contribute to a somewhat longer relaxation (37 s), of the decay of the transient jump of the permeability, observed in the permeation experiments. The temperature "histories" of suspended samples (dilation experiments) and of metal supported ones (permeation experiments) may also differ.

## CONCLUSION

Values of the estimates of  $\tau_2$ , derived from the present dilation study and from the previously reported study of the sudden increase in permeability after

decompression,<sup>1</sup> are clearly of the same order of magnitude and seem to describe related phenomena.

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