Cavity Formation on Elongation in Filled Elastomers

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Synopsis

Experiments were conducted on samples of crosslinked rubbers filled with poly(tetrafluoroethylene) powder or small glass beads. Volume changes on elongation were measured in a dilatometer. Slow deformation cycles showed considerable hysteresis, the volume on elongation being smaller than on contraction. There is much less hysteresis if the sample is degassed before the experiment. These observations suggest that, to a large extent, the volume of the cavities is determined by the availability of gases dissolved in the elastomer matrix. When the samples were saturated with carbon dioxide, nitrogen, and helium, it was indeed found that the degree of cavitation increased in order with the solubility of these gases.

The initial rate of cavitation is high. After about 1 min, dilatation is proportional to the logarithm of time. This rate is inversely related to the solubility of the gas present.

When a sample is subjected to a constant tensile stress under vacuum and the external pressure is suddenly brought to atmospheric, the elongation at first decreases due to compression of the cavities and then increases slowly as gas diffuses into them. Even unfilled compounds mixed mechanically contain submicroscopic holes. These enlarge on deformation thus causing dilatation. Only for samples prepared by evaporation from solution is there no pressure dependence of the apparent modulus.

It is demonstrated that the relation between the volume of vacuum cavities and the external pressure resembles that of volume and inflation pressure of a spherical hole in an infinite elastic medium.

INTRODUCTION

Most rubbery goods are manufactured from filled rubber compounds. Fillers are incorporated because they improve the mechanical properties of the products. The elastomer is reinforced by the filler. The extent of reinforcement depends on many factors among which perhaps the most important one is the strength of bonding between filler particles and elastomer matrix. When a rubber compound with weakly bonded filler is sufficiently deformed, the rubber matrix pulls away from the filler particles and cavities are formed oriented in the direction of the strain. Thus the volume of the material increases. This phenomenon is called cavitation, or vacuole formation. It diminishes the reinforcing effect of the filler; therefore it is of some technical importance.

The occurrence of cavitation was first demonstrated by Schippel.[1] Vac-

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uole formation was observed on stretching natural rubber containing lead shot and other filler materials. A more extensive investigation was carried out by Jones and Yiengst.[2] Volume increases up to 17% were observed in natural rubber compounds filled with barytes, zinc oxide, and other fillers. The effect of particle size, filler volume fraction, and degree of vulcanization were investigated. A strong effect of particle size was observed. The larger this size, the higher is the relative volume increase. The results are difficult to interpret quantitatively because at the high elongations imposed (up to 500%) an appreciable fraction of the polymer stress-crystallizes, as demonstrated by a decrease in volume in some experiments. Bryant and Bisset[3] reported the results of systematic investigations on natural and synthetic rubbers filled with whiting and barium, and sodium sulfate. They found a "plateau" of several hundred per cent elongation in the stress–strain curves of these materials. The mechanical response in this plateau region resembled that of a spongy material.

More recently, Oberth and Bruenner[4] investigated tear phenomena induced by stretching in filled compounds. They found that cavities are initiated at the points of highest stress which are located in the rubber matrix close to the surface of the particles. Failure of the rubber then propagates toward the particle–elastomer interface. When the crack reaches the particle surface, filler and rubber separate. This separation is called dewetting, or blanching. It was further observed that dewetting rarely occurs on both sides of the included filler particles. These observations show that bonding between particles and matrix is relatively strong in the compounds investigated by these authors. The interpretation of these and earlier results is complicated by the fact that the strength of the bonds between filler and matrix is poorly known.

In this paper we report on some investigations of cavitation on deformation of elastomers filled with poly(tetrafluoroethylene) (Teflon) particles, a filler which may be expected to bond only weakly to the rubber matrix. For comparison, some experiments are included with compounds filled with glass beads. It was found that in these compounds cavitation initiates at the filler–elastomer interface. To avoid crystallization induced by strain orientation, no elongations were imposed higher than 100%. A filler volume fraction, φ, of 0.1 was used in all experiments. This value was chosen to minimize mutual interaction of stress fields around the particles while retaining an acceptable degree of accuracy in the measurements of dilatation volume.

EXPERIMENTAL

Materials

The natural rubber used was pale crepe milled for 15 min at 30°C. It is characterized by the following data: Mooney viscosity (ML - 4', 100°C) = 38; intrinsic viscosity (toluene, 30°C) = 3.03 dl/g; solubility in toluene = 100%. Butyl rubber (Polysar Butyl 100) had a Mooney viscosity (ML

- 8', 100°C) of 45 and an unsaturation of 0.7 mole-%. The natural rubber was cured with 0.6 parts of dicumyl peroxide (Hercules Incorp.) which was recrystallized from alcohol. The curing agent for butyl rubber was 10 parts of SP 1055 resin, a condensation product of 2,6-dimethylol-4-hydro-carbyl phenols (Minnesota Mining & Manufacturing Co.). Teflon powder had an average particle size of 22 μ (E. I. du Pont de Nemours and Co.). Glass beads had an average diameter of 26 μ (Minnesota Mining & Manu-facturing Co.).

Procedures

The rubber compounds were mixed at about 70°C on a small laboratory roll mill (diam. 1 in., length 4 in.) or in a heated press as follows. The filler and curing agent were sprinkled onto a thin sheet of raw rubber. The sheet was folded twice and compressed. Folding and pressing were repeated 20 times. The natural rubber was cured in the press for 5 hr at 140°C; the curing of butyl rubber was done at 160°C for 80 min. Samples in the shape of common rubber bands were died out from the sheets. The dimensions of the bands were: circumference 127 mm, width 1.7 mm, thickness 1.2 mm.

The volume changes were determined in a dilatometer by following the meniscus in a capillary with a cathetometer. The dimensions of the capil-lary were: diameter 0.4 mm, length 25 cm. The confining oil was Silicone Fluid 100 (Dow Corning Corp.). This oil did not affect the sample. The modulus of the rubber after immersion for three weeks was within 1% of the initial value. The dilatometer was immersed in a water bath kept at 30°C. Corrections for temperature fluctuations, which were less than 0.01°C were measured with a duplicate dummy dilatometer. The sample was attached to the bottom of the dilatometer. At the upper end of the sample a small soft iron weight was fastened. For elongation, this weight was moved upward with the aid of ring magnets surrounding the dilatometer. Satura-tion with gas was achieved by bubbling the gas through the dilatometer for 24 hr. For this purpose, the dilatometer was provided with an inlet and out-let which could be sealed off.

RESULTS AND DISCUSSION

Cavitation Process and Effect of Elongation

The relation between relative volume increase of the sample and elonga-tion in a strain cycle is shown in Figure 1. The relative dilatation is indi-cated by $\Delta v = \Delta V / V$. Consecutive measurements were taken at 15-min intervals. Three features of the graph deserve comment.

First, there is an initial curvature in the extension line of the loop. After about 30% elongation, volume expansion and elongation are linearly re-lated. The initial curvature is attributed to the presence of some rubber–filler bonds such as those resulting from van der Waals forces and from
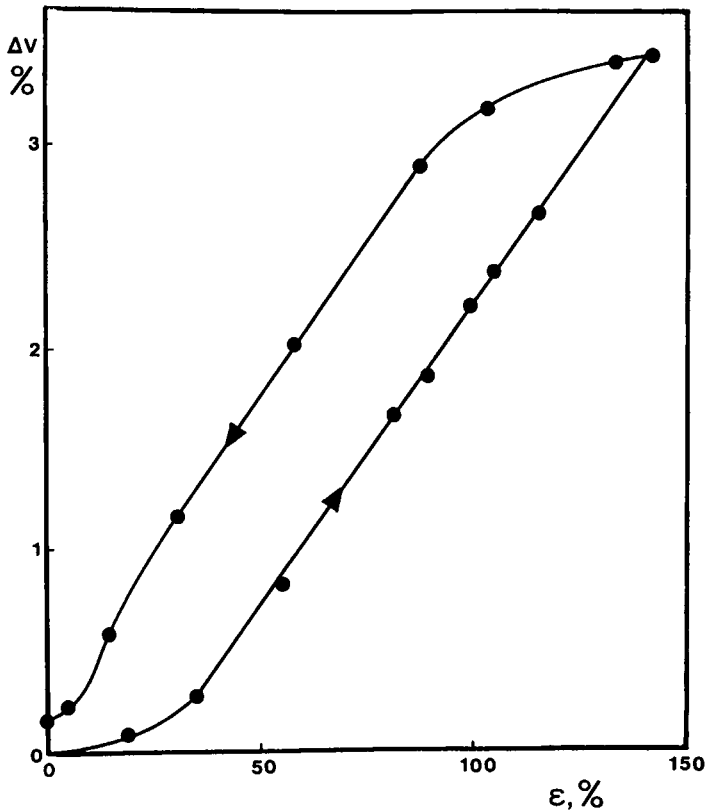
Fig. 1. Relative dilatation as a function of elongation.   Natural rubber–Teflon (10 vol-%);   chain concentration, 0.037 mole/l.;   relaxation time between measurements, 15 min.

entrapment of matrix material in surface crevices of the filler particles. To eliminate this bonding as much as possible, subsequent samples were swollen in benzene to equilibrium and dried.   They were also stretched before use to about 100% elongation and allowed to relax.   Inspection of swollen samples under the microscope showed that virtually all the particles had been completely loosened from the rubber matrix.   Under strain, cavitation occurred on both sides of the particles.

Results on a sample similar to that used for the experiment of Figure 1, but pretreated, are shown in Figure 2.   Here, the relation between volume increase and elongation is linear above about 8% extension.   Pretreatment results in diminished initial curvature of the elongation line.   Therefore, at least some of the filler–rubber bonding has been eliminated by this procedure.

Secondly, it is seen in Figure 1 that there is a considerable volume hysteresis in a strain cycle.   In stress–elongation graphs it is generally observed that retraction curves fall below extension curves, i.e., at a given elongation a smaller stress is required during retraction than on elongation.

This phenomenon of stress softening is called the Mullins' effect.[5]   It is found to occur in filled as well as in unfilled vulcanizates.   There is difference of opinion as to the cause of this phenomenon.[6]   Whatever the mechanism of stress softening is, it should result in a stress around the filler particles which is lower on retraction than on elongation.   Hence, less cavitation is expected during the retraction part of the strain cycle.   However, the opposite is observed.   This may be explained as follows.   Immediately after the application of stress, the cavities formed are vacuum pockets. Air dissolved in the surrounding elastomer diffuses into the cavities.   This process continues during all of the elongation part of the strain cycle.   On retraction, elastic forces compress the air in the cavities and the direction of diffusion is reversed.   If now the time period of 15 min allowed for relaxation between consecutive measurements is insufficient for attaining equilibrium partition of air between cavities and elastomer, then the pressure in the cavities, and hence their volume, will be larger on contraction than on elongation.   The particular shape of the retraction curve is determined by the opposing effects of gas diffusion and stress softening.   It is to be expected, and has indeed been found, that volume hysteresis is less in the second cycle.

The results shown in Figure 1 were obtained in an open dilatometer; those in Figure 2 depict the results of an experiment in which the rubber and the dilatometer were first exposed to low pressure (0.05 mm Hg) for three days after which the dilatometer was sealed off at that pressure.   The hysteresis of the partially degassed sample amounts to 25%, which is considerably less than a hysteresis of 55% for the loop of the air-saturated sample.

Thirdly, the slope of the straight line portion of the extension curve in Figure 1 (0.030) is about double that of the sample exposed to low pressure (0.017).   In the latter case, the lower gas pressure in the cavities results in a lower degree of cavitation than that of the air-saturated sample.

The presence of expandable cavities in stretched samples cannot only be seen under the microscope, but can also be demonstrated by applying vacuum to the dilatometer.   A prestretched sample of the same composition as that used in the experiment of Figure 2 was elongated by about 40% at 1 atm.   The relative dilatations of the sample measured at atmospheric pressure and also observed after an additional 1 min at 0.01 mm Hg pressure

TABLE I
Relative Dilatations of Samples

Pressure	Relative dilatation, %[a]					
	3 min	4 min	75 min	76 min	764 min	765 min
1 atm	0.38		0.77		0.93	
0.01 mm Hg		0.57		0.95		1.28
Difference		0.19		0.18		0.35

[a] Extension ratio 1.4.

are given in Table I.   It may be concluded from the data in this table that, even after a period of only 3 min, an appreciable gas pressure has developed in the cavities and that the amount of gas in the cavities increases only slowly with time.

Effect of the Nature of the Gas

Various gases have different solubilities and diffusivities in rubbers.   It is, therefore, of interest to measure cavitation in systems saturated with different gases.   Carbon dioxide, helium, and nitrogen were chosen because they differ appreciably in solubility, diffusivity, and permeability, the product of these two properties.   These properties vary somewhat with the modulus of the vulcanizate.   The data in the literature [7-11] were interpolated to correspond with the shear modulus of the samples used, namely, 2.95 and 3.1 kg/cm² for natural rubber and butyl rubber, respectively.   The values so obtained are assembled in Table II together with the solubilities

TABLE II
Solubilities, Diffusivities, and Permeabilities
of Gases in Rubbers[a]

Elastomer	Gas	Solubility,[b] cm³ (NTP) /cm³	Diffusivity, cm² sec⁻¹ × 10⁶	Permeability, cm² sec⁻¹ atm⁻¹ × 10⁶	Solubility[b] in silicone oil, cm³ (NTP)/g
Natural rubber	CO_2	0.92	1.3	1.2	1.57
	N_2	0.06	1.1	0.07	0.16
	He	0.01	22	0.24	0.04
Butyl rubber	CO_2	0.68	0.06	0.04	1.57
	N_2	0.06	0.04	0.002	0.16

[a] From references 7 to 11 (see text).
[b] Normal temperature (25°C) and pressure (1 atm).

of the gases in the silicone oil used as the confining liquid in the dilatometer.
The dilatation–time curves for natural rubber saturated with different gases are shown in Figure 3 together with the curve for a sample which was degassed by exposing the dilatometer containing the oil-confined sample for five days to a pressure of 0.01 mm Hg.   The shapes of these curves are similar.   The cavities develop in less than $^3/_4$ min, the earliest time at which readings could be taken.   Thereafter, a small additional volume increase is observed over a period of at least 75 min.   Since the initial curvatures of the lines are not the same, they do not result from stress relaxation alone.   The additional dilatation must at least in part be due to diffusion of gas into the cavities since the low pressure sample reaches an equilibrium value of $\Delta v = 1.4\%$ in 25 min.   The gas-saturated samples attain more than double the dilation of the low pressure sample in the same time period.   The volume expansions differ for different gases consistent with their solubilities.   It may be expected that, at true equilibrium,

the degree of dilatation is independent of the nature of the gas if we neglect the influence of strain on gas solubility, which is at best extremely small.[12] What differences are observed, therefore, must be the result of diffusion phenomena.

It can be seen under the microscope that the shape of the cavities is that of a cone with blunted apex.   If we assume that a cavity has the form of a cylindrical cone tangent to a spherical particle and that the distance of the apex to the center of the sphere is λ times the radius of the sphere (λ = extension ratio), it can be calculated that the relative dilatation is 2.5% for λ = 2, and φ = 0.1.   This is lower than the highest value 3.7% observed.
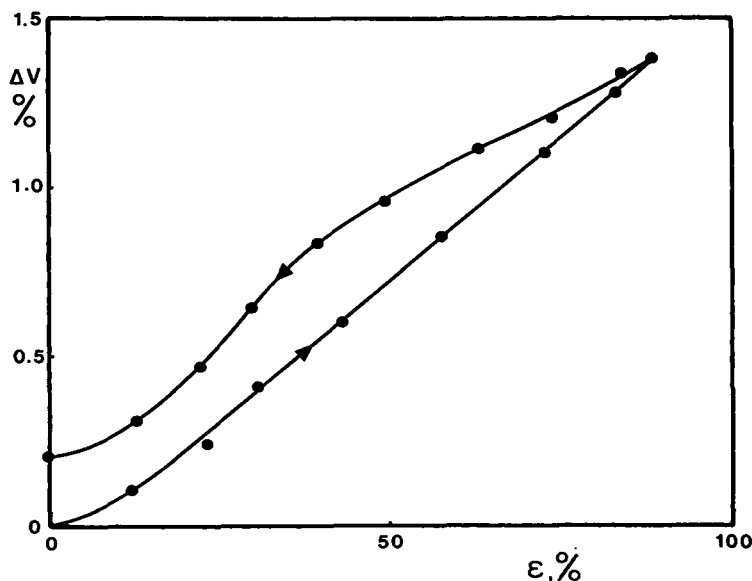

Fig. 2. Relative dilatation as a function of elongation.   Natural rubber–Teflon (10 vol-%); chain concentration, 0.035 mole/l.; relaxation time between measurements, 15 min; sample exposed to 0.05 mm Hg for three days.

Calculations for other geometric shapes give larger values for dilatation volume under the same conditions: paraboloid 6.0%, ellipsoid 10.0%.

It has been found empirically that for natural rubber compounds the volume increase of cavities up to about 20 min is linearly related to the logarithm of time elapsed since elongation.   These curves are shown in Figure 4 on an expanded scale.   For clarity, the lines have been shifted toward the abscissa over different distances.   These graphs make it possible to express the rate of the diffusion and/or relaxation process over the period 1–20 min quantitatively.   These rates and the dilatation volumes after 75 min are assembled in Table III for various systems.   The data show that each of the variables listed, namely, strain and nature of the gas, of the filler, and of the elastomer, affects rate and extent of cavitation.   The

TABLE III

Effect of Elongation and Nature of Gas, of Filler, and of Elastomer on Rate of Development and Extent of Cavitation[a]

	Elastomer	Filler	Gas	Elongation, %	Δv (75 min), %	$d\Delta v/d(\log t)$, %	$R = \dfrac{d\Delta v/d(\log t)}{\Delta v}$	No. of experiments
A-1	NR	T	N_2	20	0.45	0.045	0.10	1
-2				40	0.77	...	...	1
-3				66	1.76	0.164	0.09	2
-4				88	2.62	0.258	0.10	2
-5				100	3.13	0.300	0.10	2
B-1	NR	T	CO_2	100	3.70	0.169	0.05	4
-2			N_2		3.13	0.300	0.10	2
-3			He		2.90	0.231	0.08	2
-4			Vacuum		1.63	0.144	0.09	3
C-1	NR	T	N_2	66	1.76	0.164	0.09	2
-2		G	N_2		1.03	0.125	0.12	4
-3		G	CO_2		1.58	0.102	0.06	4
D-1	NR	T	N_2	100	3.13	0.300	0.10	2
-2	BR		N_2		2.85	$+^b$	...	4
-3	NR		CO_2		3.70	0.160	0.05	4
-4	BR		CO_2		3.19	$+^b$	...	4

[a] NR, Natural rubber; BR, butyl rubber; T, Teflon; G, glass beads.
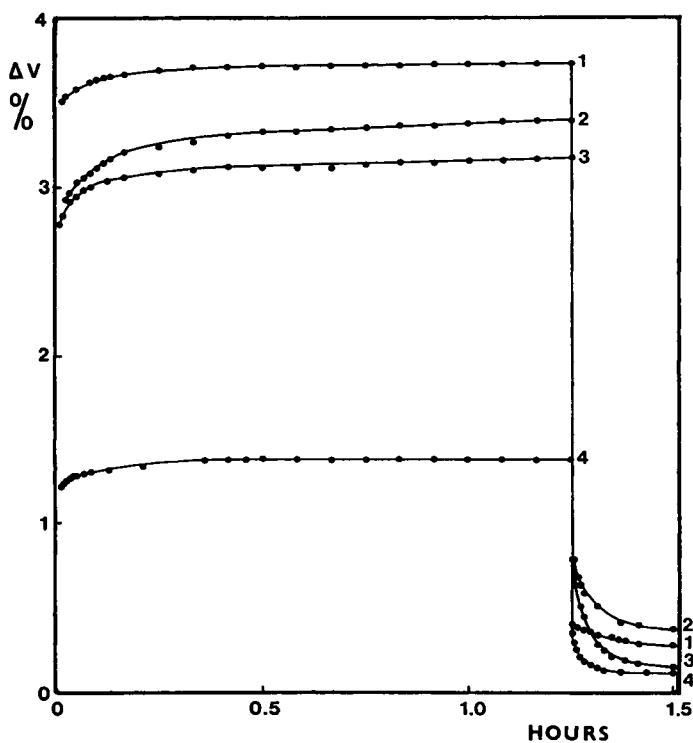[b] Samples exhibited appreciable creep.

Fig. 3. Dilatation–time curves. Natural rubber-Teflon (10 vol.%); chain concentrations, 0.035–0.038 mole/l.: (1) carbon dioxide; (2) nitrogen; (3) helium; (4) after exposure to 0.01 mm Hg for five days.

reproducibility of the experimental results can be judged from the typical set of data in Table IV. Comments on reproducibility will be made below.

It can be seen from Table III (samples A-1 to A-5) that cavitation increases linearly with elongation, as was also observed in the experiments shown in Figures 1 and 2. By comparing different gases dissolved in the same rubber (B-1 to B-3; C-2, C-3; D-2, D-4), it is noted that the higher the solubility of the gas, the greater is the dilatation after 75 min and also the initial degree of cavitation (cf. Fig. 3). Apparently, there is an initial

TABLE IV
Rate of Development and Extent of Cavitation.
Reproducibility of Experiments.[a]

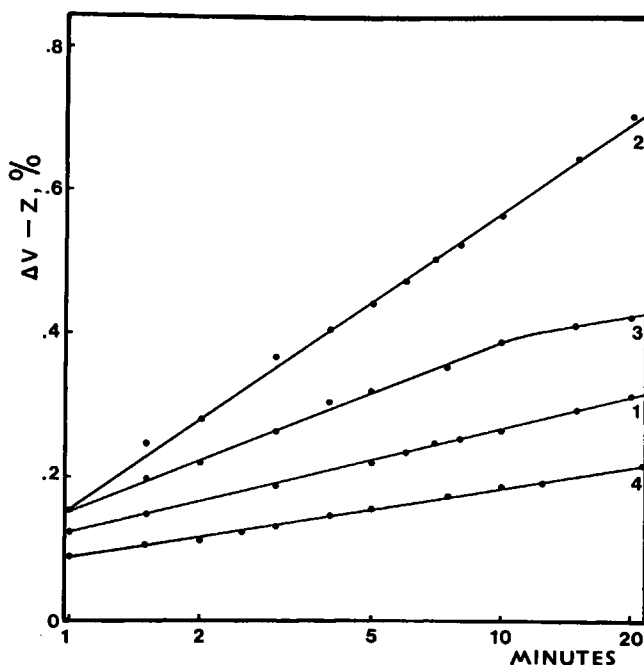| Experiment	Δv (75 min), %	$d\Delta v/d$ (log t), %
1	3.73	0.188
2	3.74	0.177
3	3.40	0.148
4	3.95	0.162
Average	3.70	0.169

[a] Extension ratio 2; gas, CO_2.

Fig. 4. Dilatation–log time curves. Natural rubber–Teflon (10 vol-%); chain concentrations, 0.036–0.038 mole/l.: (1) carbon dioxide, $z = 3.38\%$; (2) nitrogen, $z = 2.68\%$; (3) helium, $z = 2.56\%$; (4) after exposure to 0.01 mm Hg for five days, $z = 1.15\%$.

influx of gas into the cavities immediately after these vacuum pockets are formed. The amount of gas rushing in is mainly determined by its solubility in the matrix material. It may be expected that the pressure in the cavities shortly after their formation depends, furthermore, on the inverse of their volume. The rate of subsequent dilatation is inversely related to this pressure. Therefore, the larger the cavity volume, the higher should be the rate of volume increase. The data in Table III show that there is indeed a close relation between these two quantities. In fact, the ratio R (rate/volume) is remarkably constant independent of elongation (samples A-1 to A-5) and type of filler (C-1, C-2; B-1, C-3).

Once the gas concentration in the rubber immediately surrounding the cavities is reduced, the rate of further dilatation depends on the rate of gas supply from more remote elastomer. This rate is governed by three factors, viz., the pressure already developed in the cavities, their surface area, and the permeability of the gas. Comparing nitrogen and carbon dioxide, we note that the relative rates R are 0.10 and 0.05, while the permeabilities of these gases are 0.07×10^6 and 1.2×10^6 cm^2 sec^{-1} atm^{-1}, i.e., the rates vary far less than do the permeabilities, and in inverse order. This can only be the case if the initially developed pressure of carbon dioxide is far closer to the equilibrium value than that built up by nitrogen. This is consistent

with the much higher solubility of carbon dioxide (0.98 cm^3/cm^3) compared to that of nitrogen (0.06 cm^3/cm^3).   These solubilities should be considered relative to the observed dilatation, which is about 0.03 cm^3/cm^3.

Effect of External Pressure

To investigate the effect of external pressure on cavity volume, experiments were conducted (A) at constant stress and (B) at constant elongation.

Constant Stress

In the creep-type experiment (Fig. 5A), a constant load was applied to the sample elongated to about $\lambda = 2.2$ under a pressure of 0.01 mm Hg. After 421 hr, when the creep rate of the weakly crosslinked sample (chain concentration 0.035 mole/l.) was steady, the vacuum was released, exposing the sample to atmospheric pressure (see upper insert in Fig. 5).   The sample contracted immediately as the external pressure compressed the cavities and then slowly extended to elongations higher than those under vacuum due to diffusion of air into the vacuoles.   This diffusion takes place at a low rate; only after about 70 hr did creep attain its original rate.

As a control, the same experiment was conducted on an unfilled sample. A similar behavior is observed, though the effect of pressure change was
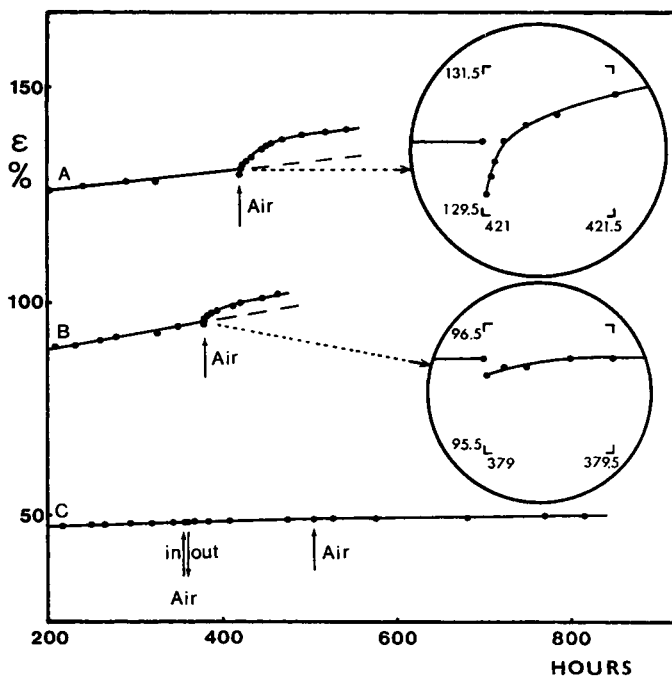

Fig. 5. Elongation–time curves.   Natural rubber: (A) filled, Teflon (10 vol-%); (B) unfilled, sample and curing agent mixed in press; (C) unfilled, sample prepared by evaporation from solution.

less pronounced (Fig. 5B and low insert). It is concluded that unfilled samples also develop cavities, even though inspection under the microscope showed very few visible bubbles. The cavities presumably form from tiny gas pockets present in the raw elastomer or included in the rubber during sample preparation. This conclusion is in agreement with that of Gent,[13,14] who found evidence for submicroscopic holes in experiments of a different nature.

In order to eliminate entrapped gas, a third sample was prepared as follows. Polymer and curing agent were dissolved in benzene. The solution was removed by slow evaporation at room temperature. The resulting film was cured at 130°C. (The modulus of this film was higher than that of previous samples mainly because of free access of air to the film during cure.) No bubbles could be detected in this sample when viewed under the microscope. The same experiment as described above was performed (Fig. 5C). After 360 hr, air was admitted to the elongated sample and was pumped out $^3/_4$ hr later. The sample was again exposed to atmospheric pressure after an additional period of 144 hr. No change in elongation was observed during any of the pressure changes.

It follows that samples prepared by dispersing filler and curing agent on a laboratory mill or in a press (see experimental section) and cured under low pressure contain nuclei for cavitation. This, of course, gives rise to poor reproducibility. This problem was encountered early in the investigation. By standardizing sample preparation procedure, reproducibility was improved to an acceptable level (see Table IV).

In general, air entrained in raw rubber or entrapped during compounding may well account for the usually poor reproducibility of mechanical properties of rubber compounds.

Constant Elongation

In the experiments described hitherto, it was found that the volume of the cavities varies with the unknown pressure of the gas inside them. In order to obtain a quantitative relation between dilatation and pressure, cavitation volume was measured of a gas-free sample as a function of external pressure over a short period of time which is insufficient for gas to diffuse through the confining oil to the sample. It had been observed previously that it is difficult to degas a sample completely when it is immersed in the silicone oil inside the dilatometer. Even after exposure to 0.01 mm Hg for five days, gas bubbles formed at the rubber–oil interface on elongation. For the experiment described below, the sample and the oil were degassed separately at 0.01 mm Hg for seven days. Also the oil was kept at 100°C. The sample was elongated by 100%, and the external pressure was increased in steps, at 10-min intervals, from 0 to 1 atm. The amount of gas that could diffuse to the sample through the oil in the long capillary tube is negligible because, on repetition of the experiment with $1^1/_2$-hr time intervals between pressure changes, the volume changes were only very slightly more.
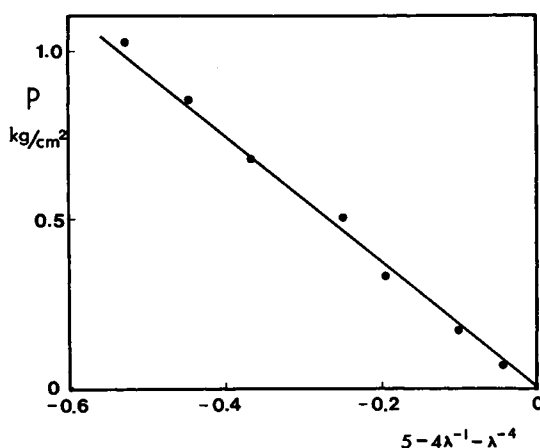
Fig. 6. Relation between external pressure and a function of dilatation volume (see text). Natural rubber–Teflon (10 vol-%); chain concentration, 0.040 mole/l.; extension ratio, 2.

For the evaluation of the results, it is assumed as a first approximation that the cavities respond to pressure changes as do spherical holes in an infinite elastic medium. The relation between the external pressure P and the radius of a vacuum hole is given by $-P = \frac{1}{2}G\,(5 - 4\lambda^{-1} - \lambda^{-4})$, where G is the shear modulus and λ is defined as the ratio of the radius at zero external pressure to that at pressure P.[15] Here, this ratio is calculated from dilatation volume: $\lambda = [(\varphi + \Delta v_0)/(\varphi + \Delta v_p)]^{1/3}$, where φ is the volume fraction of the filler and Δv is the relative volume increase.

In Figure 6, the function $(5 - 4\lambda^{-1} - \lambda^{-4})$ is plotted against external pressure. The slope of the line in this plot is 1.8 kg/cm². From stress–strain measurements, a value of $\frac{1}{2}G = 1.5$ kg/cm² was obtained for an unfilled specimen prepared from the same rubber-curing agent mix as that used for the filled samples. These two values are in reasonable agreement, in spite of the simplicity of the model of spherical cavities which does not take the effect of tensile stress into account.

CONCLUSIONS

The experimental results presented lead to the following conclusions:

On deformation of filled compounds with weakly bonded fillers, cavitation is initiated at the particle–elastomer interface. Gas dissolved, in the elastomer diffuses into the vacuum pockets thus formed.

The initial degree of dilatation is mainly determined by the solubility of the gas. It is tentatively suggested that the observed low rate of further dilatation is mainly governed by the difference in the initially developed pressure inside the cavities and the external pressure.

Even unfilled compounds mixed mechanically contain submicroscopic gas pockets. These enlarge on deformation, thus causing cavitation. The

entrapped gas may well account for the usually poor reproducibility of mechanical properties of rubber compounds. In assessing the results of elastic property measurements, the possible effects of cavitation must be considered.

The relation between volume of vacuum cavities and external pressure resembles that of volume and inflation pressure of a spherical hole in an infinite elastic medium.

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