Volume change and gas transport at uniaxial deformation of filled natural rubber*

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The volume dilatation of differently filled specimens of natural rubber has been measured using a deformation dilatometer. If the matrix detaches from the filler particles, hollow spaces form. The volume dilatation caused by this effect can be measured and calculated if the material is submerged in a liquid medium. The measured volume dilatation reflects the interaction between filler and matrix. If we take a measurement in a gas, only the volume dilatation of the matrix is recorded, but not that of the visible hollow spaces, because gas can diffuse from the measurement chamber into the sample. Stress-induced crystallization occurs with all samples. Its course due to deformation has been examined using a deformation calorimeter. Here an influence of the interaction between filler and matrix has been found. Filler particles which do not adhere closely to the matrix enhance the diminution of locally high tensions and deformations and thus hinder the stress-induced crystallization. The volume contraction caused by stress-induced crystallization can be recorded clearly only if one uses a liquid as the measurement medium. Due to gas exchange between the sample and its environment and the different gas solubilities in the amorphous and crystalline material no stress-induced crystallization can be detected. At the same time, a possibility opens up of determining gas solubilities in crystalline material.

1. Introduction
In technology, filled polymers are of great importance. Their application properties are determined, among other things, by the interaction of filling material and matrix, by the interaction of the material and its environment, and by the occurrence of stress-induced crystallization.

We have investigated these phenomena using a deformation dilatometer. The volume changes of various crosslinked specimens of natural rubber have been measured at uniaxial deformation. The comparison of materials having different fillers and filler contents is very instructive. We have also examined unfilled materials as samples with a modified interaction of filler and matrix caused by the use of bonding agents.

Compared to their importance up to now, only a few investigations of this kind have been carried out (e.g. [1-7]).

2. Experimental technique
The deformation dilatometer which we use has been described several times already [8, 9]. This instrument records the volume change at uniaxial deformation. During the measurement the sample is in a closed chamber which can be filled with liquids up to a certain height so that the specimen is completely submerged. Volume changes of the sample change the gas pressure within the chamber, above the liquid's surface. This pressure change is recorded. At the same time the tensile force is registered. We have taken measurements in argon, air and mercury.

The samples were stretched in steps of approximately 20%. After each deformation step we waited about 90 min. By reason of the resulting slow deformation rate of about 0.22% min^{-1} the specimen is in a state of equilibrium, because thermal effects have decayed and the restoring force has relaxed to a constant value before a value is recorded.

The relative error of the measurements is approximately 10%.

3. Specimen materials
We have examined six different specimens of natural rubber, which have been crosslinked with dicumyl peroxide (DCP) (2.4 wt %). Two samples were filled with glass beads (3.4 vol %), two others with silicic acid (4 vol %). In one case each, the filler particles were coated with a bonding agent. As a bonding agent aminopropyltriethoxisilane was used for the glass beads, and bis-(3-tiethoxypropyl-)tetrasulphide for the silicic acid.
materials were produced by Chemische Werke Hüls AG (Marl, W. Germany). A further sample containing glass beads (20 vol %) was provided by Bayer AG (Leverkusen, W. Germany).

The specimens were stored in the same gas (air and argon) in which they were measured afterwards. The samples which were examined in mercury had been stored in air.

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*Dedicated to Professor Dr F. H. Müller on the occasion of his 80th birthday.
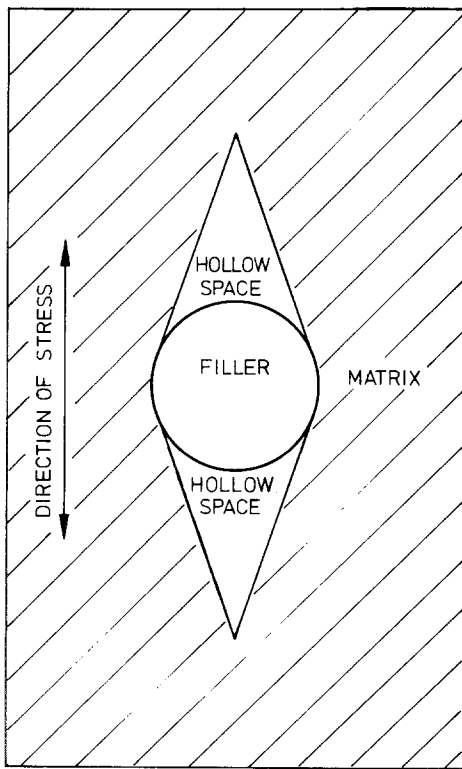
Figure 1 Shape of the hollow spaces forming during deformation.

4. Theory

If the matrix does not adhere to the filler particles, cone-shaped hollow spaces form on both sides in the direction of the deformation (Fig. 1). This is proved by microscopical investigations. The hollow spaces enlarge their volume due to increasing deformation, i.e. the sample volume grows. This growth may easily be calculated [10] as

$$\left(\frac{\Delta V}{V_0}\right)_{\text{Hollow space}} = \frac{\phi}{2}\left(\lambda + \frac{1}{\lambda} - 2\right) \qquad (1)$$

where $\Delta V/V_0$ is the relative volume enlargement, λ the deformation ratio and ϕ the filler content by volume. This formula is approximately valid for non-spherical particles, too, if their geometrical anisotropy is not too strong.

In this formula, the filler content is the only parameter. The number and size of the filler particles do not matter. The correctness of this calculation presupposes the forming of the hollow spaces on all particles upon the beginning of the deformation. Usually, this is not so. The number of the hollow spaces grows due to increasing deformation as can be seen from microscopical investigations. Therefore, Equation 1 has to be multiplied by a growth function $\psi(\lambda)$ which describes the increasing number of hollow spaces due to deformation. This growth function is specific to the particular matrix–filler system. Moreover, the volume dilatation of the unfilled matrix must be added to the volume enlargement which has been calculated in this way. We obtain the following expression for the total volume enlargement:

$$V_{\text{total}} = \frac{\phi}{2}\left(\lambda + \frac{1}{\lambda} - 2\right)\psi(\lambda) + \left(\frac{\Delta V}{V_0}\right)_{\text{Matrix}}$$

The growth function is given by

$$\psi(\lambda) = \frac{1}{\sigma(2\pi)^{1/2}}\int_1^{\lambda_g} [-(\lambda' - \lambda_m)^2/2\sigma^2]\, d\lambda'$$

where σ is the width of the Gaussian function and λ_m the maximum of the Gaussian function, i.e. the deformation ratio for the strongest increase of the number of hollow spaces. By fitting the measured course of the volume dilatation we obtain values for λ_m and σ.

Yilmazer and Farris [7] obtain an expression for the volume dilatation of the samples they have examined by a twofold integration over a Gaussian function. They do not give any statements concerning the volume enlargement of existing hollow spaces. In contrast, our paper is based on an expression for the volume enlargement of existing voids. The growth in number of hollow spaces is also described by an integration over a Gaussian function. Therefore our starting point is completely different from that of Yilmazer and Farris.

5. Measurements and results
5.1. Microscopical investigations
As a preliminary experiment, we stretched the specimens and observed the formation and growth of the voids using a microscope. In Fig. 2, an undeformed (Fig. 2a) and a deformed (Fig. 2b) sample are compared. The photo of the stretched sample clearly shows cone-shaped hollow spaces on both sides of the filler particles. The number and size of these voids increase due to increasing deformation. With the specimen containing a bonding agent, this increase is evidently slower.

5.2. Investigations using the deformation calorimeter
We examined all samples using a deformation calorimeter to get detailed information about their stress-induced crystallization.

In the deformation calorimeter, the heat tone and the tensile force of the sample are measured. From the force the deformation work is calculated. According to the First Law of Thermodynamics, the change of internal energy at each deformation step is equal to the difference between heat and work. If materials which show ideal entropy elasticity are deformed, internal energy does not change:

$$\Delta U = 0$$

From a certain deformation ratio the decrease of ΔU indicates stress-induced crystallization of the real rubber. Fig. 3 shows the crystallization behaviour of the different samples measured in the deformation calorimeter.

As can be easily seen, the specimens filled with silicic acid start crystallizing at a deformation ratio slightly less than 100%. The samples filled with glass beads start crystallizing at a slightly higher deformation. Here, the decrease of internal energy due to deformation occurs at a much slower rate than with materials containing silicic acid. At the same deformation ratio, there is a definitely smaller crystallinity.
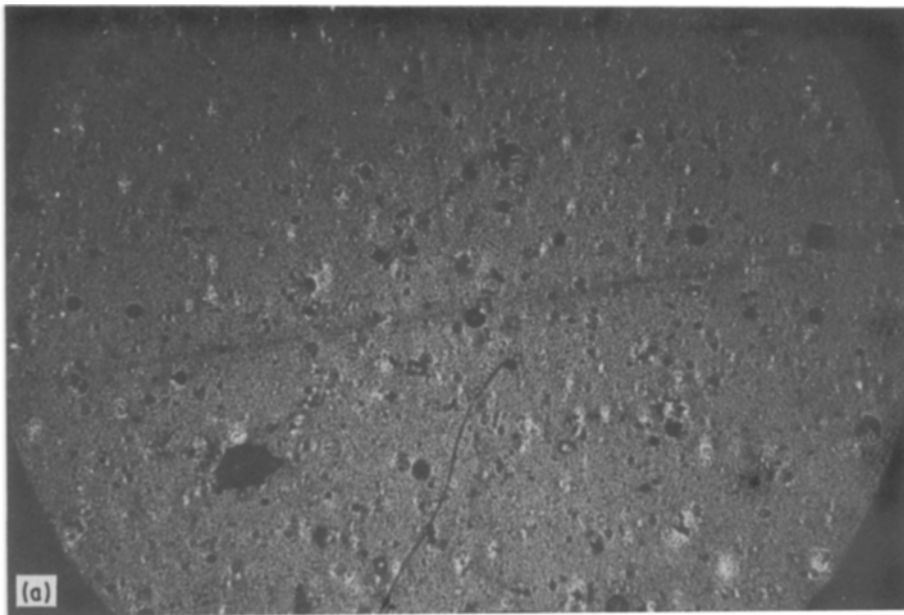
The unfilled sample lies between the substances filled with silicic acid and glass beads.

5.3. Dilatometer measurements

First we measured the volume change of the different specimens in mercury. Within the examined deformation range, the specimens filled with glass beads show a volume dilatation of a few per cent, which can be described very well by the theory we have introduced above (Fig. 4).

The volume dilatation of the sample containing a bonding agent is very small at the beginning. The dilatation measured up to 140% deformation corresponds to that of an unfilled sample. At this point a marked enlargement of the sample volume occurs.

Being measured in mercury, the specimens filled with silicic acid show only a small volume dilatation up to deformations of about 140%, which again corresponds to that of an unfilled matrix (Fig. 5). At higher deformation ratios the volume enlarges more and more, but it does not reach the value of glass-filled

samples. Differences between the substances with and without bonding agents cannot be detected in this case.

In Fig. 6 we compare the volume dilatation of filled specimens measured in air with the dilatation measured in mercury. In air, the sample volume dilates by only a few parts per thousand. It is remarkable that the sample having a glass bead content of 3.4% shows the same volume dilatation as a sample having the sixfold filler content, i.e. 20%.

In Fig. 7 we compare the volume change of a filled specimen in argon to that of an unfilled one in mercury. Up to a deformation of 200% both measurements show practically the same results. At higher deformations the unfilled substance shows a strong volume contraction.

6. Conclusions

6.1. The interaction between filler and matrix

Being stretched in mercury, the filled samples show a volume dilatation which can be calculated. From the
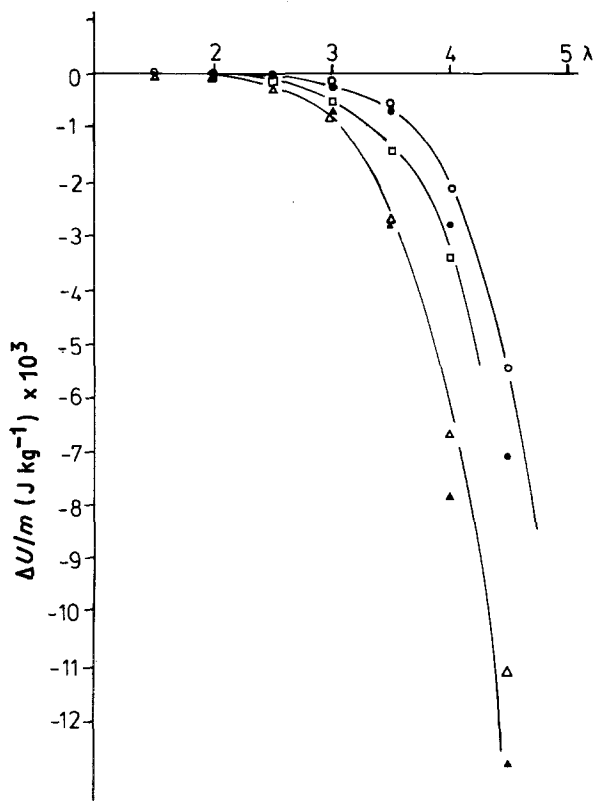
Figure 3 Deformation calorimeter measurements of different samples of crosslinked natural rubber: change of internal energy ΔU due to deformation. ($\square$) Unfilled, ($\bigcirc$) glass beads without bonding agent, ($\bullet$) glass beads with bonding agent, ($\triangle$) silicic acid without bonding agent, ($\blacktriangle$) silicic acid with bonding agent.

course of the volume dilatation and from the fitting parameters of the calculation we can draw conclusions concerning the interaction between filler and matrix.

The incipient small volume enlargement of the samples containing glass beads and bonding agent is evidence for a strong adhesion of filler and matrix in this deformation range. Therefore, only a few hollow spaces form in the beginning. Before a deformation of about 140% is reached no change can be seen. The two curves seem to be shifted relative to each other by more than 50% along the deformation axis. This is reflected in the λ_m values of 2.7 and 3.5 in the theoretical calculation. When at last hollow spaces have formed

on all filler particles, and when their growth in size is correlated with the deformation ratio in the same way as it is with the sample containing no bonding agent, both specimens are supposed to show the same volume dilatation at sufficiently high deformation ratios. A convergence of both the curves is seen in Fig. 4 above $\lambda \approx 4$. But here the theory differs from the measurements. Therefore, we will not go on discussing this phenomenon.

The volume dilatation of the substances filled with silicic acid does not reach the values of the glass-filled ones, though they are comparable with regard to the filler content. From this we draw the conclusion that the maximal number of hollow spaces has not yet formed at the deformation we have reached. This means that the adhesion of the silicic acid particles and the matrix is generally strong. Therefore, it is immaterial whether the materials do contain a bonding agent or not. They behave in the same way. The strong adhesion can be seen from the theoretical λ_m value of 4.3, which is above the values for the glass-filled specimens.

6.2. The interaction between the specimens and their environment

The volume dilatation measured in a gas is much smaller than that which has been measured in mercury. Moreover it is independent of the filler content. Hence it follows that only the volume enlargement of the matrix can be recorded, if one uses a gas as the measurement medium. The microscopically visible voids induced by filler particles are not recorded. This can be explained as follows by the interaction of the samples with the gas atmosphere (Fig. 8).

Gas — first dissolved in the matrix — streams into the hollow spaces, which form during the deformation process. Since there is less gas dissolved in the matrix than normally corresponds to the solubility, gas diffuses from outside into the sample to be dissolved there. The disappearance of gas out of the measurement chamber compensates for the pressure increase caused by the volume dilatation. Only the volume enlargement of the matrix is measured. On the other hand, if the sample is submerged in mercury, no gas
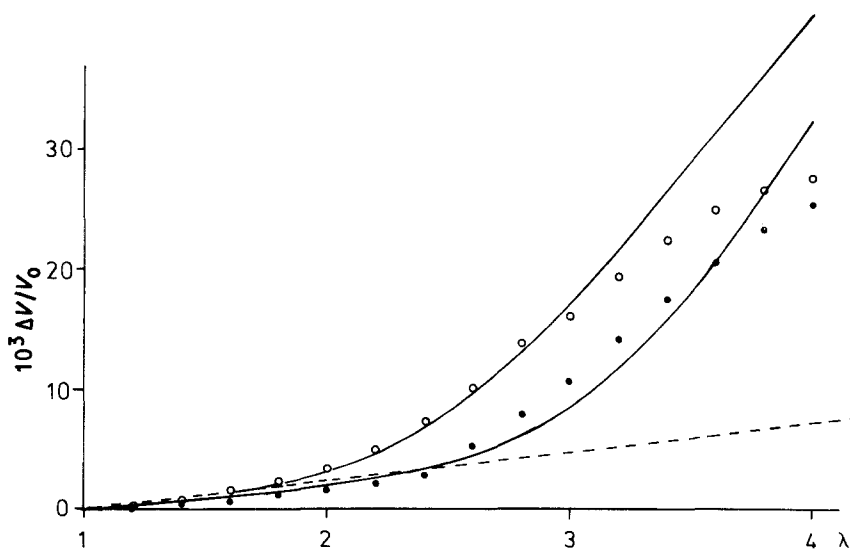

Figure 4 Volume dilatation of materials filled with glass beads; measurements in mercury and calculations. Fitting parameters in both cases $m = 0.0025$, $\sigma = 0.8$ and $\lambda_m = 2.7$ (containing no bonding agent), $\lambda_m = 4.3$ (containing a bonding agent). ($\bigcirc$) Without bonding agent, ($\bullet$) with bonding agent, (– – –) unfilled, (——) theory.
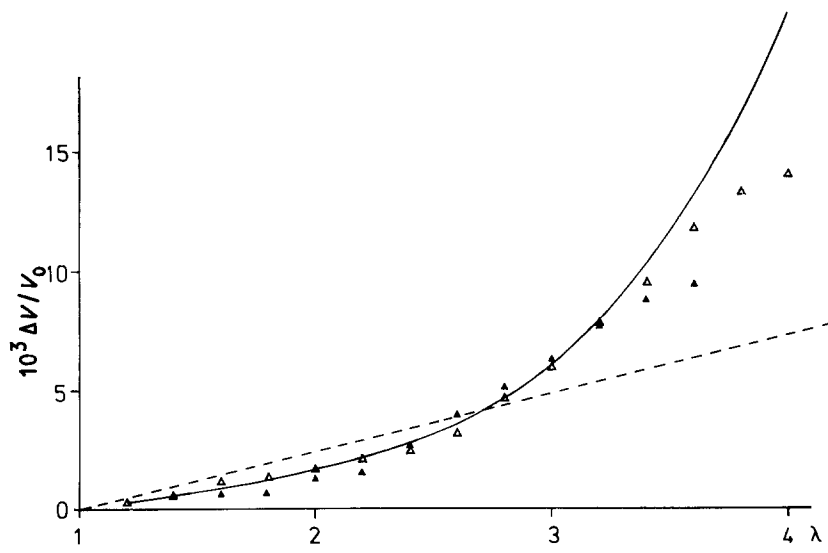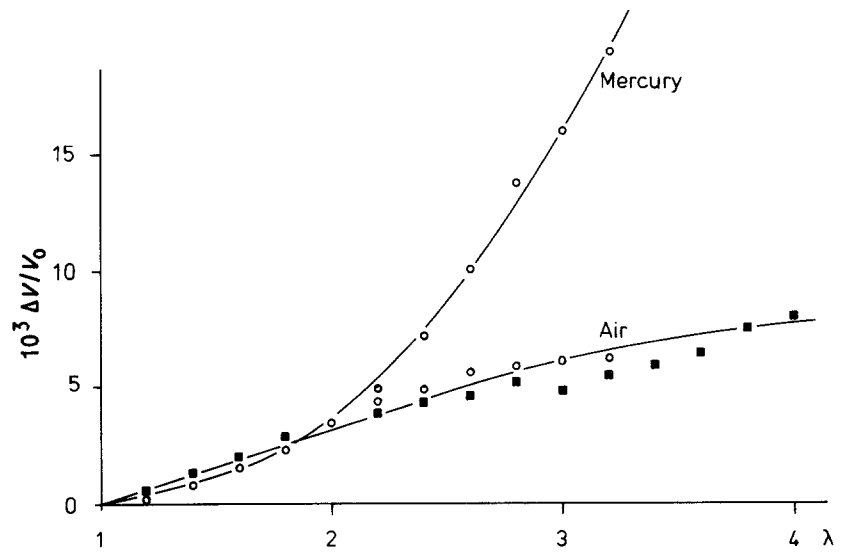
Figure 6 Dilatometer measurements in air and mercury: samples contain (O) 3.4 and (■) 20 vol % glass beads. No bonding agent added.
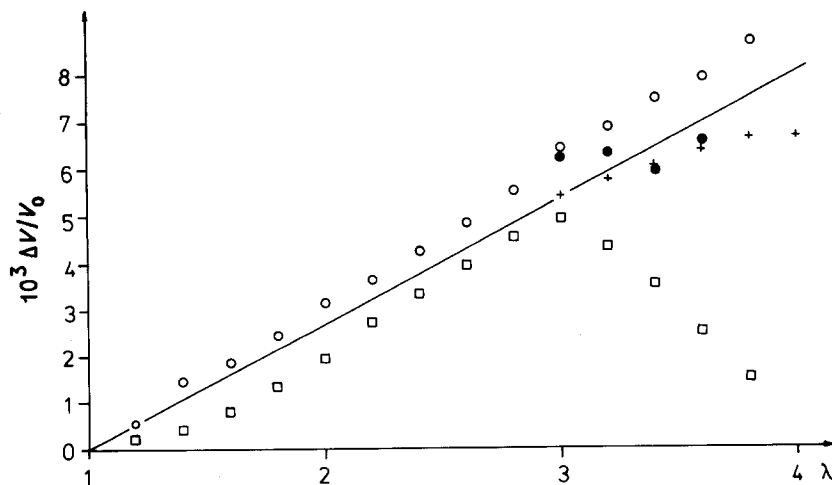

Figure 7 Dilatometer measurements; (O) sample containing glass beads in argon and (□) unfilled sample in mercury. Values in air: (●) measured, (+) expected, containing glass beads.
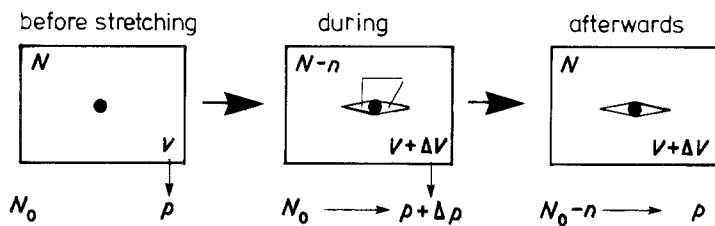
Figure 8 Proceedings during dilatometer measurement of filled sample in gas. N = number of gas molecules inside the sample, N_0 = number of gas molecules inside the chamber, n = number of gas molecules diffusing into the hollow spaces, V = volume of the sample before stretching, ΔV = volume change of the sample, p = pressure within the chamber, Δp = pressure change within the chamber caused by the volume change of the sample.

can diffuse from its environment. All contributions to the volume dilatation are recorded.

6.3. Stress-induced crystallization

Being examined in the deformation calorimeter, all substances show stress-induced crystallization. It is supposed to occur mainly in sample regions locally more stressed than their surroundings [9, 11]. Rigid filler particles closely adhering to the matrix enhance local tension peaks and support the forming extremely stretched regions [9, 11]. On the other hand, fillers which do not adhere closely diminish the tension peaks. Since the matrix easily detaches itself from the filler particles, in their surroundings no states of extreme deformation can occur. Therefore the interaction of filler and matrix, as recorded with a dilatometer, is reflected by the crystallization behaviour due to the deformation. The diminution of extreme tensions and deformations by non-adhering fillers is so pronounced that this material crystallizes still more slowly than that of the unfilled matrix.

In practice, no differences between materials with and without bonding agents are ascertainable. With regard to the samples filled with silicic acid, this confirms the results from dilatometer measurements that — in this case — the bonding agent causes no essential additional effect. With the samples filled with glass beads the differences in the crystallization behaviour, especially at the beginning of crystallization, cannot be seen because of the insensitive plotting of Fig. 3. At high deformation significant differences are no longer found, since in this case a lot of hollow spaces form which diminish the tension peaks. These hollow spaces do form even within samples containing a bonding agent, as can be seen from dilatometer measurements.

Crystallization causes a volume contraction counteracting the volume enlargement. Contrary to that which is expected this is perceivable in only one case, that is the measurement of the unfilled specimen in mercury.

Regarding the other measurements, no volume decrease can be seen. Using the degree of crystallinity (deformation calorimeter measurement) and the known density difference of about 10% between amorphous and crystalline material [12, 13], we can calculate the volume contraction which is supposed to overlay the enlargement. It amounts to a few parts per thousand and is small compared to the volume enlargement caused by the fillers. Examining filled specimens in mercury, their volume contraction cannot be recorded with the accuracy of measurement. On the other hand, this is comparable to the volume dilatation of the matrix measured in gas with all samples. Here it

should be easily perceived, but also in gas no volume decrease is measured.

This discrepancy shows us that the volume contraction caused by stress-induced crystallization is clearly recordable in a liquid, but not in a gas as the measurement medium. For this we propose the following explanation based on the different solubilities of the gases we used as measurement media in the crystalline and the amorphous materials.

On account of their storing conditions the specimens are saturated with the gases used. The gas solubilities for crystalline materials are much smaller than those for amorphous ones [14]. We could find exact values for amorphous substances [15].

Amorphous regions of natural rubber reduce their own volume by about 10% when crystallizing. This causes a corresponding pressure decrease within the measurement volume of the dilatometer. At the same time, the originally amorphous material sets free the gas, which is no longer dissolvable during the crystallization. Since the uncrystallized material is already saturated with gas, excess gas is given off to the measurement volume if the sample is in a gas atmosphere. This causes a pressure increase within the measurement chamber counteracting the decline in pressure caused by crystallization.

In the case of argon, the pressure decrease caused by crystallization is exactly compensated by the gas coming out of the sample. Only the volume dilatation of a non-crystalline matrix is measured. The solubility of argon in amorphous natural rubber amounts to about $0.13\,\text{bar}^{-1}$ ($1.3\,\text{MPa}^{-1}$) under standard conditions [15]. In the crystalline material it is supposed to be smaller by about $0.1\,\text{bar}^{-1}$ ($1\,\text{MPa}^{-1}$). Hence the volume of argon given off amounts to 10% of the originally amorphous, now crystallized, volume fraction of the sample.

In air, we observe a flattening of the volume-deformation curve at higher deformations (Fig. 5). Therefore, the volume of the gas coming out of the sample is too small to compensate for the volume contraction due to crystallization. This is a consequence of the smaller solubility of air compared to argon. It amounts to $0.07\,\text{bar}^{-1}$ ($0.7\,\text{MPa}^{-1}$) [15] in amorphous material. Using this value and the known degrees of crystallinity, the solubility of air in crystalline natural rubber can be calculated from the difference between the volume measurements in argon and in air. On the other hand, if we assume a certain value for this, we can calculate the volume dilatation in air starting from the measurement in argon. Assuming that air does not dissolve at all in the crystal, we achieve a good coincidence with the measurement (Fig. 7).

On account of the limited accuracy of measurement and the small number of readings this is of course only a rough method, but at least there is a possibility of estimating gas solubilities in crystals. Another contributory factor may be that different gases are adsorbed differently at inner surfaces forming during deformation. Such an effect has been found with natural rubbers filled with carbon black [9], where air is more strongly adsorbed than argon.

If there is mercury but no gas within the measurement chamber, the transport of gas out of the sample is drastically hindered. The pressure in the interior of the specimen increases, and the gas which is no longer soluble in crystalline regions dissolves under the enhanced pressure in the amorphous regions of the sample. Hence the volume contraction due to stress-induced crystallization can be measured clearly in principle only if one uses a liquid as the measurement medium.

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