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Strain-Rate Dependent Stress-Strain Properties of Solution Crosslinked Poly(Isobutylene)-Networks

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Abstract: Poly(isobutene) networks (butyl rubber) have been prepared by solution crosslinking. Networks have been characterized by swelling and mechanical measurements. The strain rate dependent stress strain behaviour is discussed in terms of a time dependent network unfolding process.

INTRODUCTION

Crosslinked polymers above their glass transition temperature show rubber elastic behaviour, i.e. they combine the properties of high reversible deformability with at low stress level. Since the description of long chain molecules by gaussian chain statistics (1), various theories have been published to describe the mechanical properties of rubbery networks by a molecular theory (see references given in 2,3,4). All of these theories consider a strained elastomeric network in equilibrium, i.e. no time dependent changes are considered. Parallel to the improvement in the theoretical description of rubberlike materials, neutron scattering (5) and deuterium NMR spectroscopy (6) provide more detailed information on the deformation behaviour on the molecular level. The experimental results reported so far indicate, that the assumptions of the theories with respect to the orientation behaviour are oversimplified. More complicated deformation mechanisms as network unfolding or inhomogeneous deformations along a network chains should be taken into account. The introduction of the domain of constraints can account for all experimental findings.

The nonequilibrium properties of elastomers are of great technological interest. In real rubber networks it is very difficult to achieve stress equilibrium. In recent work it has been pointed out, that the modes of motions of dangling ends in elastomeric networks are very slow (7), much slower than the relaxation of free draining chains in the network. Kramer has given a survey on the experimental work to describe the contribution of dangling ends on the relaxation of rubber networks(8). Such slow modes of motion also could arise from arrangements of the network chains, as has been discussed from neutron scattering experiments(9) and D-NMR (6).

To give a consistent description of the properties of elastomeric networks, equilibrium as well as nonequilibrium properties must be considered. In this paper the results of strain rate dependent stress strain measurements on butyl rubber networks are reported. From such experiments one should be able to obtain information about the time dependent topological rearrangements in elastomeric networks.

THEORY

Stress strain measurements on crosslinked elastomers can be analyzed in terms of the phenomenological Mooney-Rivlin equation (10). where the reduced force $[f] = f/(\lambda - 1/\lambda^2)$, f being the measured force per unit area of unstrained sample and λ the extension ratio with respect to the unstrained length.

In equilibrium studies, the Mooney Rivlin constant $2C_1$ has been identified with the modulus of the phantom network. However there is experimental evidence that there is also a contribution of topological interactions on $2C_1$ and not only on $2C_2$.

The phantom modulus G_{ph} is related to molecular parameters according to

$$G_{ph} = \frac{1}{2} \nu_e R T \frac{\langle r^2 \rangle}{\langle r^2 \rangle_0} \qquad \text{-1-}$$

where ν_e is the density of elastically effective chains in the dry network in mol/cm^3 and $\langle r^2\rangle/\langle r^2\rangle_0$ is the memory term, the ratio of the average dimensions of the network chains in the unstrained state and the reference state where the network is formed.

According to the Boltzmann superposition principle (11), the stress response of a crosslinked elastomer at small strains can be expressed by

$$\sigma(\varepsilon,t) = E^{\infty}\varepsilon(t) + \int_{\infty}^{t} G(t-t')\,\dot{\varepsilon}(t-t')\,dt' \qquad \text{-2-}$$

where E^{∞} is the equilibrium modulus, $\varepsilon(t)$ the strain history, G(t) the relaxation function and $\dot{\varepsilon}(t)$ the derivative of the strain function. This equation is valid as long as there is a linear relationship between stress and strain. From stress relaxation experiments at high extensions it has been shown (12), that the response of a elastomeric material can be described by a time- and a strain dependent function.

$$\sigma(\lambda,t) = G(t) * f(\lambda) \qquad \text{-3-}$$

For a certain strain, the stress reponse functions only differ by a constant factor. As will be seen below, the stress strain experiments for the different strain rates can be described by the MOONEY-RIVLIN equation. In this case, both $2C_1$ and $2C_2$ must be considered to be time dependent and the time dependence may be different. If $2C_1$ only contains information about the density of the network as implied by application of equation 2 the influence of topological constraints should be inherent in $2C_2$. Consequently viscoelastic relaxation processes then should be restricted mainly to $2C_2$.

EXPERIMENTAL

Technical grade poly(isobutene) (butyl rubber) (Me = 400000) has been used as elastomer. Crosslinking was performed in solution using 4,4'-methylen-bis-(1,4-phenylene)-di-1,2,4-triazoline-3,5-dione, synthesized according to literature prescriptions (13). Crosslinking was carried out in toluene or THF solution (polymer concentration = 5 wt.-%). Films for mechanical measurements were obtained by spin casting of the reaction mixture before the reaction reaches the reaction threshold. Films where dried in vacuo. Strips of 30x5mm^2

were cut and put into the clamps of a INSTRON 1122 tensile testing machine, equipped with a birefringence device (14).

In addition, swelling measurements have been performed in toluene at different temperatures. The swelling data where analyzed according to the FLORY-REHNER theory (15).

RESULTS AND DISCUSSION

CHARACTERIZATION OF THE NETWORKS

Two sets of networks were prepared by performing the crosslink reaction either in toluene or in THF which is a bad solvent for butyl rubber. From temperature dependent swelling experiments in toluene the Flory-Huggins interaction x parameter was determined to be 0,37 for the samples obtained in toluene and 0,39 for the samples crosslinked in THF. In figure 1 the number of elastically effective network chains as obtained from equilibrium swelling measurements is plotted versus the calculated number of network chains. Both types of networks show the same behaviour, indicating that the state of the polymer chains in the semidilute region where the crosslinking has been carried out is the same for both solvents. From the slope of this plot the size of the memory term (see eq. 2) is determined to 0,23. This value is much larger than would be predicted from the concentration where crosslinking has been performed. The same result is obtained from mechanical measurements at stress equilibrium (from $2C_1$ according to equation 2). Here in addition the samples with very low crosslink density are included for which no swelling experiments were carried out. The value for the memory term is the same as from swelling experiments.

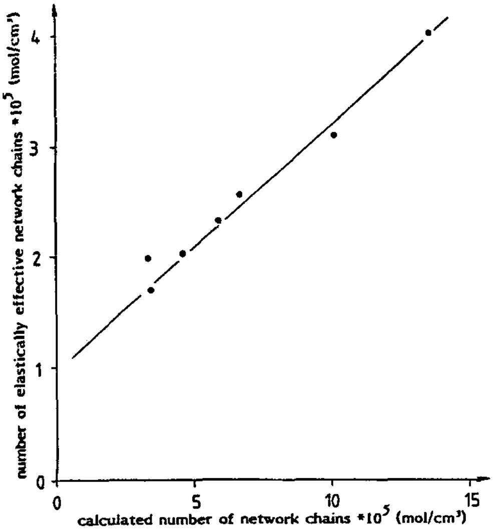


fig. 1: experimental versus calculated number of crosslink junctions; experimental data from swelling measurements

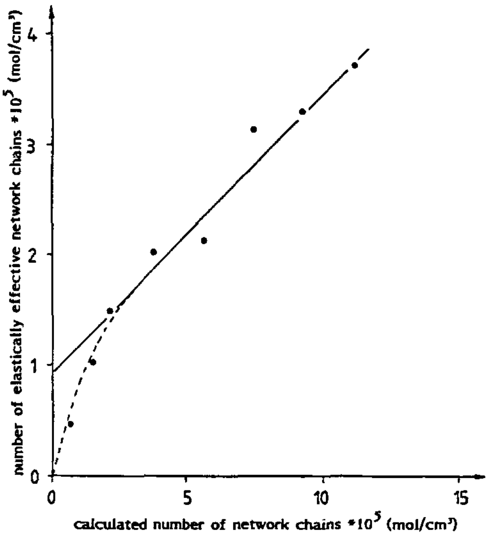


fig. 2: experimental versus calculated number of crosslink junctions; experimental data from mechanical measurements

The finite intercept indicates the contribution of permanent entanglements to the network(11). A similar behaviour is found for solution crosslinked polybutadiene networks (16,17) where additional effects due to the occurence of elastically ineffective loops must be taken into account. The separation between ineffective loops and the memory factor can be made from the analysis of birefringence data (17).

STRAIN RATE DEPENDENCE

For all samples and strain rates (0,1 - 20 mm/min), linear MOONEY-RIVLIN plots were obtained. Only at very low deformations (1/λ → 1) deviations could be observed, which can be attributed to difficulties in determining the unstrained length. Errors of about 0.02 mm will cause significant curvature in this region. Therefore effects at 1/λ larger than 0.9 will not be considered here. In figure 3 the MOONEY RIVLIN plots of some samples are given for different crosslink densities for a strain rate of 20 mm/min. Obviously at small strains, the sample with low crosslink density shows a larger modulus. This effect turns out more clearly in fig.4 where the initial slope of the stress strain curve (YOUNG modulus) is plotted versus the crosslink agent concentration.

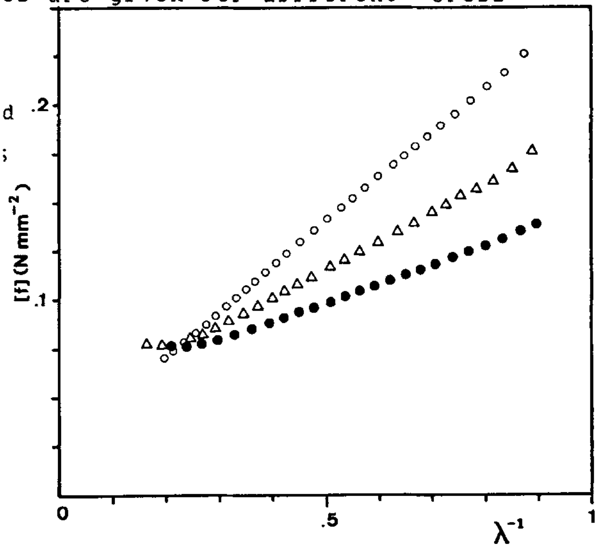


fig.3
Mooney-Rivlin plot (reduced force versus 1/λ) for different crosslink densities; strain rate of 20 mm/min

crosslink densities

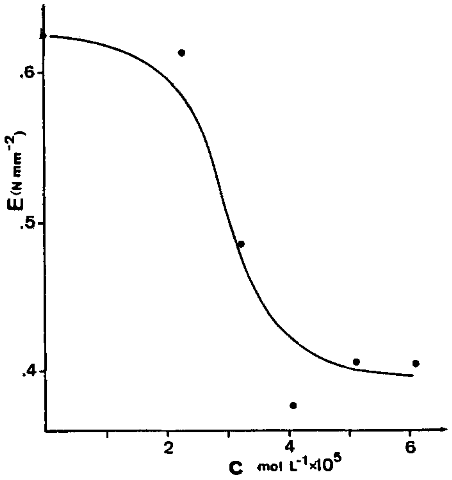
$6.06*10^{-5}$ mol/cm^3: ●

$4.2*10^{-5}$ mol/cm^3: △

$2.33*10^{-5}$ mol/cm^3: ○

fig.4:

Young modulus E (N/mm^2) from the initial slope of stress strain measurements at strain rate 20 mm/min as a function of the concentration of crosslinking agent



The effect, that at low strains and high strain rates the uncrosslinked sample shows the highest modulus is an indication of the strong influence of temporary topological constraints on the stress-strain behaviour of rubbers.

In figure 5 the $2C_1$ and $2C_2$ values for different butyl rubber networks are collected as a function of the strain rate. The basic results to be drawn from this figure are:

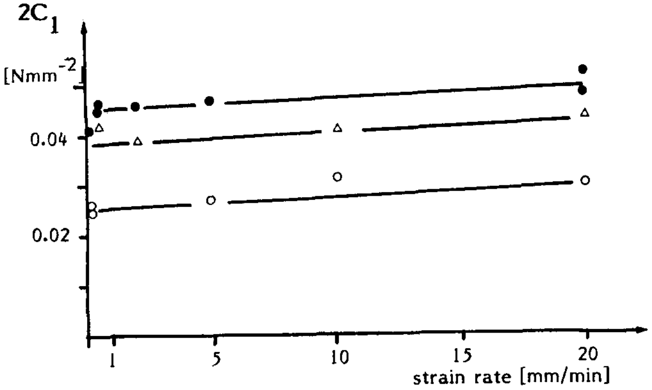
1. $2C_2$ is much more dependent from the strain rate than $2C_1$

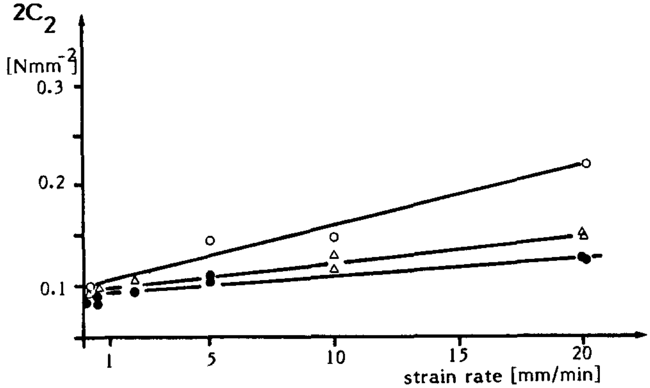
2. There is a small strain rate dependence of $2C_1$

3. The strain rate dependence of $2C_2$ depends on the crosslink density, while the strain rate dependence of $2C_1$ is the same for all samples.

4. From extrapolation to strain rate zero, the same value of $2C_2$ for the different networks is obtained, while 2C1 reflects the different chemical crosslink density.

fig. 5: Dependence of the Mooney Rivlin constants from the strain rate for butyl rubber networks of different crosslink density; the symbols are the same as in fig. 3





These results may be understood in terms of the different network topology of the samples. Because the crosslinking was performed under identical conditions for all samples, the differences in the strain rate dependent behaviour must arise from differences in the structure of the bulk entangled polymer, that arise upon deswelling of the formed highly swollen gels.

In highly crosslinked samples the network chains are imposed to more restrictions and on deswelling the degree of interpenetration of the chains is less than in samples of low crosslink density. These consequently show larger values of the stress at low tensions and high strain rates where the temporary entanglements are contributing to the overall stress.

According to literature results (10), for strain rate zero, the slope $2C_2$ is the same for all networks. An interesting feature of the networks is the relatively large value of $2C_2$ compared to $2C_1$. According to the theory, $2C_2$ should be smaller than $2C_1$ and reach $2C_1$ for the affine limit. In the present networks the $2C_2$ is larger (2-3 times) than $2C_1$ depending on the crosslink density even for extrapolation to zero strain rate. Similar results have been reported recently for natural rubber, PMMA and PVAc networks (18).

The low strain rate dependence of $2C_1$ on the other hand indicates that topological restrictions - temporary and peramanent - only contribute to a minor degree to $2C_1$. This is not in contradiction to the results of figures 1 and 2, that permanent entanglements contribute to the modulus.

The different strain rate dependencies could be interpreted in more detail by applying the Boltzmann superposition principle (eq. 3). For the large strains, the consitutive equations of linear viscoelasticity are no more applicable and an empirical approach corresponding to the Mooney-Rivlin equation appears to be promising on the basis of the experimental results presented in this paper:

$$\sigma(\lambda,t) = (2C_1(t) + 2C_2(t)/\lambda)(\lambda^2 - 1/\lambda) \qquad -4-$$

For both $2C_1$ and $2C_2$ additivity of time dependent and equilibrium contributions is assumed

$$2C_i(t) = 2C_i^0 + 2C_i'(t) \qquad -5-$$

For experiments at a constant strain rate the time dependence has to be taken into account and an equation similar to eq. 3 is obtained for nonlinear behaviour:

$$\sigma(\lambda,t)=(2C_1^0 + 2C_2^0/\lambda)(\lambda^2-1/\lambda) + \int_{-\infty}^{t} 2C_1'(t-t')\,\frac{d(\lambda^2-1/\lambda)}{dt'}\,dt' + \int_{-\infty}^{t} 2C_2'(t-t')\frac{d(\lambda-1/\lambda^2)}{dt'}$$

The first term corresponds to the equilibrium situation described by the Mooney-Rivlin equation (eq. 1). The basic difference compared to eq. 3 is the occurence of two integrals with different strain dependence. Substituting λ by the strain rate $\lambda = vt' + 1$ the integrals have the form

$$\int_{-\infty}^{t} 2C_1'(t-t')\,[2v(vt'+1)+(vt'+1)^{-2}]\,dt' \text{ and } \int_{-\infty}^{t} 2C_2'(t-t')[v+v(vt'+1)^{-3}]\,dt'$$

$2C_1' + 2C_2'$ can be interpreted as the stress relaxation modulus at small strains. For the butyl rubber networks the integrals should be equal to a constant x strain rate (according to fig. 5). A more detailed analysis will be given in a subsequent paper.

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References:

1) Kuhn W., Kolloid Z. 1934, 68, 2
2) Guth E., James H.M., Ind. Eng. Chem., 1941, 33, 624
3) Flory P.J. Principles of Polymer Chemistry, 1953, New York, Cornell University Press, pp. 434 - 440
4) Flory P.J., Proc.R.Soc.London, A, 1976, 351, 351
5) Candau S., Bastide J., Delsanti M., Adv. Polym. Sci. 1982, 44, 27
6) Gronski W., Stadler R., Jacobi M.M., Macromolecules 1984, 17, 741
7) Curro J.G., Pincus P., Macromolecules 1983, 16, 559
8) Kramer O., British Polym. J., 1985, 17, 129
9) Ullman R., Macromolecules 1982, 15, 582
10) Treloar L.R.G., ‘The physics of rubber elasticity’, Clarendon Press, Oxford 1975
11) Ferry J.D., ‘Viscoelastic properties of polymers’ 3rd. ed, John Wiley & sons, New York 1980
12) Chasset R, Thirion P, Proc.Conf.on Physics of Non-Crystalline Solids, J.A.Prins ed., North Holland Publishing, Amsterdam 1965
13) Cookson R.C., Gupte S.S., Stevens J.D.R., Watts C.T., Org. Synth. 1971, 51, 121
14) Bühler F., Stadler R., Gronski W., Makromolekulare Chemie, submitted for publication
15) Flory P.J., Rehner J., J.Chem.Phys., 1943, 11, 512
16) Stadler R., Jacobi M.M., Gronski W., Makromol.Chem., Rapid Commun. 1983, 4, 129
17) Stadler R., Bühler F., Gronski W., Makromol.Chem., submitted for publication
18) Mitchell G.R., British Polymer Journal, 1985, 17, 111

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