Elastic Behavior of Natural Rubber Filled Vulcanizates

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Synopsis

The reinforcement effect of carbon black and, the effect of accelerator-to-sulfur ratio variation on the elastic behavior of natural rubber vulcanizates have been studied. The Mooney–Rivlin relation was used to describe the behavior of the rubber matrix, and values of constants c_1 and c_2 have been evaluated with the use of the strain-amplification factor. The stress softening of the vulcanizates tested has also been examined.

INTRODUCTION

The mechanism by which carbon black reinforces elastomers in relation to the state of cure is one of the most interesting problems of modern technology. In spite of an ambiguity in defining the term reinforcement, it is now generally agreed that reinforcement is an effect by which abrasion resistance, tear strength, and tensile strength are simultaneously improved.[1] On the other hand, reinforcement is almost always observed to occur together with some undesirable effects in the rubber compound, such as increased relaxation and creep rates, compression, or tensile set and hysteresis. Many studies have been published describing one aspect or another of the behavior of carbon black.[2]

Payne[3] reported that the state of cure and the particle size of a given filler may also affect the deformation mechansims of filled elastomers. In another work, the dependence of hysteresis on carbon black loading has been examined.[4]

In an attempt to develop a quantitative physical basis for the increased stiffness and strength of vulcanized rubber by the addition of fine particulate fillers, mainly the effect of fillers on elastic behavior has been studied. Theoretical expressions relating the elastic modulus E of the filled rubber to the modulus E_0 of the matrix have been derived.[5]

For spherical filler particles at low concentrations Smallwood[3] showed that

$$E = E_0(1 + 2.5c) \tag{1}$$

where c is the filler volume concentration.

Guth and Simha[6] and Gold[7] by taking into account the interaction between neighboring filler particles added an extra term as follows:

$$E = E_0(1 + 2.5c + 14.1c^2) \tag{2}$$

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Smallwood[3] showed that eq. (1) fitted the elastic behavior of rubber containing nonreinforcing or lightly reinforcing fillers, but serious departures occured with more highly reinforcing fillers.

Guth and Simha[6] found that eq. (2) confirms to the behavior of rubber reinforced with thermal carbon black up to volume concentrations 0.3.

The departures observed at higher concentrations were due to the tendency of carbon blacks to agglomerate into chainlike clusters.

Therefore, he proposed the relation

$$E = E_0(1 + 0.67fc + 1.62f^2c^2) \tag{3}$$

where f is a factor describing the asymmetric nature of the aggregated clusters as expressed by the ratio of their length to width.

However, some difficulties arise by using the above theoretical relations. One of them is due to the continuously increasing value of the strain after application of the stress, and it is then necessary to have an equilibrium value of the strain corresponding to a certain period for a given stress. Another difficulty concerns the softening which occurs as a result of previous stretching. Because of this softening, large changes in the shape factor f are required.

In this work the effect of carbon black as well as the variation of chemical crosslinking of natural rubber due to the increasing function of accelerator-to-sulfur ratio on the elastic behavior of the vulcanizate have been studied.

MATERIALS

Four mixtures of the same natural rubber SIR20 (supported by GoodYear Hellas) have been used. In all four kinds of samples, the components are the same except the accelerator content. As an accelerator a sulfenamide, 2-morpholinothiobenzothiazole, or MBS has been used, with its content varying as follows: Compound no. 1, 0.45 phr; no. 2, 0.50 phr; no. 3, 0.60 phr; and no. 4, 0.70 phr. The natural rubber in all blends is 61.7%, the carbon black of the type ISAF N220 is 26.5%, ZnO 2.5%, and S 1.54%.

Moreover, pure natural rubber designated as type-0 with accelerator MBS content 0.40 phr and the same sulfur concentration has been tested. The curing conditions are 32 min at 150°C.

EXPERIMENTAL

Stress–strain measurements were made in simple extension on dogbone specimens of an average cross-sectional area (1.9 × 6) mm^2. Reference marks were made on each specimen about 36 mm apart and clamps applied to both ends. The measurements were carried out with a conventional Instron type 1121 tester at room temperature, at a crosshead speed of 5 mm/min.

The distance between the reference marks was measured with a cathetometer 15 min after each application of load. In this period the sample achieved an approximately equilibrium extension.

RESULTS AND DISCUSSION

Equilibrium stress–strain measurements as described above have been carried out for all types of vulcanizates tested. These data are presented in

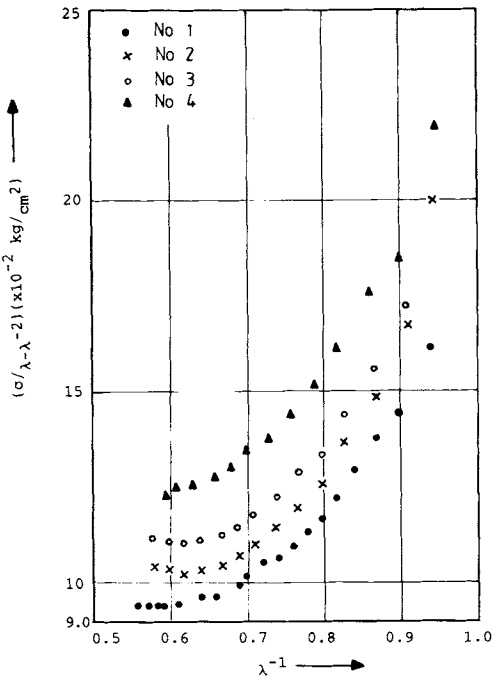

Fig. 1. Stress–strain curves plotted as $\sigma/(\lambda - \lambda^2)$ against λ^{-1} of four types SIR-20 vulcanizates reinforced with ISAF carbon black type N220.

Figure 1, following the Mooney–Rivlin equation

$$f\left[2A_0(\lambda - \lambda^{-2})\right]^{-1} = c_1 + c_2\lambda^{-1} \tag{4}$$

where f is the force required to maintain the sample at an extension ratio λ, A_0 is the unstrained cross-sectional area of the sample, c_1 is a term pertaining to ideal elastic behavior, and c_2 is a term which expresses departures from ideal elastic behavior.

The stress–strain behavior of natural rubber vulcanizates at large deformations can conveniently be described by the Mooney–Rivlin equation. Each of the curves show a linear relation over a range of low and moderate extensions, having an intercept on the axis $\lambda^{-1} = 0$ of c_1 and a slope of c_2.

As it is obvious from Figure 1 all the experimental stress–strain curves show pronounced curvature. Therefore, the estimation of constants c_1 and c_2 becomes difficult.

In Figure 2 these curves are replotted with the use of the strain-amplification factor X, which takes into account both the disturbance of strain distribution and the absence of the deformation of fillers.[5] The tendency of carbon blacks to agglomerate into chainlike clusters is also taken into account, and this factor X is given by

$$X = \sigma/\epsilon E_0 = E/E_0 = 1 + 0.67fc + 1.62f^2c^2 \tag{5}$$

where ϵ is the strain produced by stress σ and E_0 the modulus of the matrix, meaning that the local strains are on average X times greater than the overall strain.

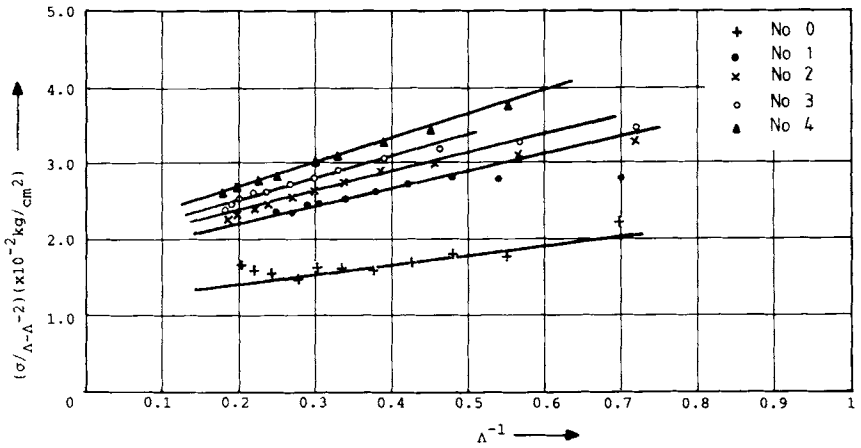

Fig. 2. Stress–strain curves of Figure 1 replotted with the use of the strain-amplification factor.

This reasonable assumption requires that the extension ratio λ in eq. (4) appropriate to the rubber matrix should be calculated from the measured overall strain by putting

$$\lambda = 1 + X\epsilon \tag{6}$$

This value of extension ratio will be designated as Λ.

The value of the shape factor f in eq. (5) was chosen to be 6.9 for the best fitting to the experimental data.

The use of the strain amplification factor X results in a linear portion of the Mooney–Rivlin plots by means of $f[2A_0(\Lambda - \Lambda^{-2})]^{-1}$ against Λ^{-1} in a range of moderate and low deformations.

From these plots the constants c_1 and c_2 have been determined and presented in Table I for the four different cases of accelerator content. As observed from Table I, there is an increase of 17% for constant c_1 as the accelerator content increases, resulting in a higher degree of crosslinking and a much higher increase about 45.5% for constant c_2.

TABLE I
Values of Constants c_1 and c_2 Obtained from Stress–Strain Curves with Use of Strain-Amplification Factor, for First and Second Stretching Cycles

Sample type Compound no.	MBS (phr)	Measured values ($kg/cm^2 \times 10^{-2}$)			
		First cycle		Second cycle	
		c_1	c_2	c_1	c_2
0	0.40	1.15	1.26	0.90	1.10
1	0.45	1.77	2.27	1.75	1.65
2	0.50	1.90	2.44	1.83	1.82
3	0.60	1.95	2.94	1.90	2.31
4	0.70	2.07	3.20	1.95	2.80

The constant c_1 describes the behavior predicted by the statistical theory of rubberlike elasticity and its value is directly proportional to the number of network chains per unit volume of the rubber. As observed, the ratio of accelerator to sulfur has an important influence on the degree of crosslinking[8] and consequently on the value of constant c_1.

The constant c_2, which appears to be slightly higher than c_1, is also an increasing function of the degree of crosslinking. The molecular origin of c_2 is not exactly known, and up to now it is considered to be an empirical constant.

The value of c_2 may be determined by the number of steric obstructions and the number of the effectively elastic trapped entanglements, as well as other network defects.[9] The dependence of constant c_2 in a simple way to the topological contribution has been established experimentally very well by the work of Dossin and Graessley.[10]

Polybutadiene networks of well-characterized primary chains have been tested under stress–strain behavior, suggesting that trapped chain entanglements constitute a possible contribution to c_2.[11]

Following the above remarks, the reason that c_2 of filled vulcanizates is higher than that of the pure matrix is now obvious. In the case of filled systems, because of the neighboring of the filler particles to the rubber matrix, effects such as steric obstructions or topological distribution and other network defects become serious. Due to the same effects, c_2 is an increasing function of the acceleration content (degree of crosslinking).

Another indication of the reinforcing potential of fillers in relation to the different degree of crosslinking of the vulcanizates is the softening that occurs in carbon-black-filled rubber vulcanizates upon stretching, retraction, and subsequent extensions. This phenomenon, the Mullins effect,[5,11] has been the subject of several investigations.

The vulcanizates tested, after an initial stressing at a strain rate of 5 mm/min at room temperature were retracted. The samples were allowed to relax for a few minutes and then they were stretched for a second time. The Mooney–Rivlin plots of the second stressing cycle are presented in Figure 3

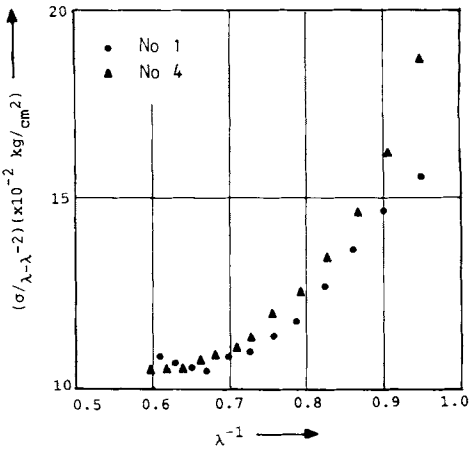

Fig. 3. Stress–strain curves obtained in the second stretching cycle for samples type-1 and type-4.

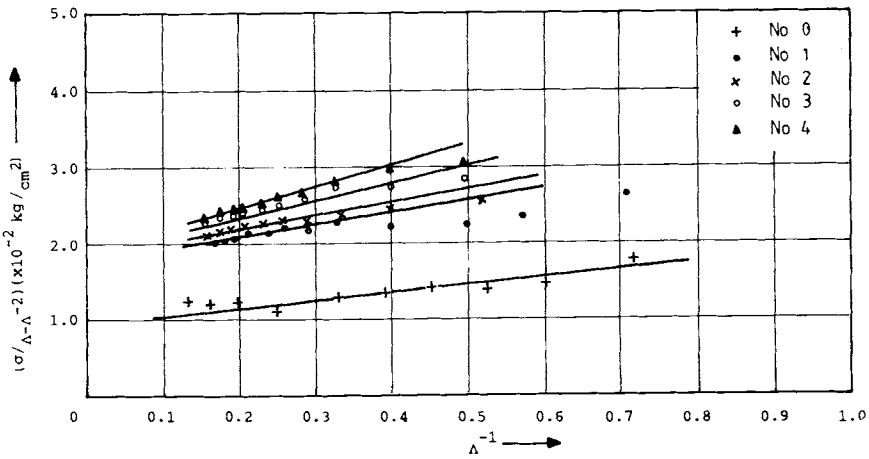

Fig. 4. Stress–strain curves of Figure 3 replotted with the use of the strain-amplification factor.

representatively for types 1 and 4 while the data of sample types 2 and 3 are between them. These data with the use of the strain-amplification factor X are replotted in Figure 4. From this figure the softening process is obvious, especially for the samples with the highest accelerator content.

Values of constants c_1 and c_2 obtained in the second stressing cycle are presented in Table I. These values appear now to be lower than those from the first stressing cycle. This is a reasonable effect, because the stress softening that occurs mainly during the first deformation, has been attributed to the breakage of agglomerates, or to the breakage of weak bonds between the rubber and the carbon black surface.[12]

The reduction of constants c_1 and c_2 is due to the fact that the attachment between rubber molecules and carbon black particles has a contribution to the rubber network, acting as a physical crosslink. The breakdown of this attachment after the first stressing cycle results to a decrease of the total (physical and chemical) crosslink density of the rubber–carbon black system.

References

1. Zri Rigbi, *Rubber Chem. Technol.*, **55**, 1180 (1982).
2. G. Kraus, *Angew. Makromol. Chem.*, **60 / 61**, 215 (1977).
3. A. R. Payne, in *Reinforcement of Elastomers*, G. Kraus, Ed., Wiley-Interscience, New York, 1965, p. 76.
4. J. D. Ulmer, W. M. Hess, and V. E. Chirico, *Rubber Chem. Technol.*, **47**, 729 (1974).
5. L. Mullins and N. R. Tobin, *J. Appl. Polym. Sci.*, **9**, 2993 (1965).
6. E. Guth and R. Simha, *Kolloid Z.*, **74**, 266 (1936).
7. O. Gold, thesis, University of Vienna, 1937.
8. M. Porter, T. D. Skinner, and M. A. Wheelans, *J. Appl. Polym. Sci.*, **11**, 2271 (1967).
9. L. S. Priss, *J. Polym. Sci., C*, **53**, 195 (1975).
10. L. M. Dossin and W. W. Graessley, *Macromolecules*, **12** (1), 123 (1979).
11. G. Kraus and G. A. Moczygemba, *J. Polym. Sci.*, **A 2**, 277 (1964).
12. J. A. C. Harwood, L. Mullins, and A. R. Payne, *J. Appl. Polym. Sci.*, **9**, 3011 (1965).

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