

Effect of Fillers on the Viscoelastic Behavior of Rubbers

B. STENBERG and J. F. JANSSON, *Department of Polymer Technology, The Royal Institute of Technology, Stockholm, Sweden*

Synopsis

The different reinforcing effects of carbon blacks are determined by measurements of the linear and nonlinear viscoelastic behavior of natural rubber samples subjected to prestrains at different levels. The transition from linear to nonlinear viscoelastic behavior occurs at lower strains as the carbon black content is increased. At a given filler concentration, the limiting strain is highest for the most reinforcing carbon black. Prestraining increases the limiting strain. The reinforcing effect of carbon black can be estimated by determining the extent to which prestraining influences the linear viscoelastic properties of vulcanizates.

INTRODUCTION

The theoretical basis for the analysis of the linear viscoelastic behavior of polymers has been extensively discussed by Yannas.¹⁻⁴ Linear viscoelastic behavior of polymers can be determined from isochronous stress-strain diagrams, as shown in Figure 1. The upper curves are obtained when relaxation experiments are carried out at different strains. The lower curve is obtained when corresponding σ and ϵ values at the chosen time t_1 are plotted against each other. This lower curve is the isochrone for time t_1 . Up to the point ϵ_L, σ_L , an approximately linear relationship holds. Above this point, deviation from linearity is noticed; ϵ_L and σ_L are called respectively the limiting strain and the limiting stress.

The limiting strain and limiting stress are temperature dependent, and Yannas³ has shown that the limiting strain increases very sharply when T_g is exceeded. Strain limits observed below T_g are usually reported in terms of the strain function $\ln \lambda$, where λ is the ratio of the extended to the original specimen length, whereas observations made several degrees above T_g are reported in the form $1/3(\lambda^2 - \lambda^{-1})$, which is familiar from the equation of state for ideal rubbers. The latter strain function is negligibly different from $\ln \lambda$ at small strains. In Yannas' reviews,^{3,4} the reported strain limits are shown as $1/3(\lambda^2 - \lambda^{-1})$; below T_g , the strain limits fall in the range 0.1-10%, whereas the limits in the rubbery state fall in the range 10-100%.

The linear viscoelastic behavior of rubbers has earlier been discussed by Yannas,^{3,4} Tobolsky,⁵ and Bartenev and Lyalina.^{6,7} We now report a study of the different reinforcing effects of SAF and Thermax MT based on measurements of the linear and nonlinear viscoelastic behavior of rubber samples subjected to prestrain at different levels.

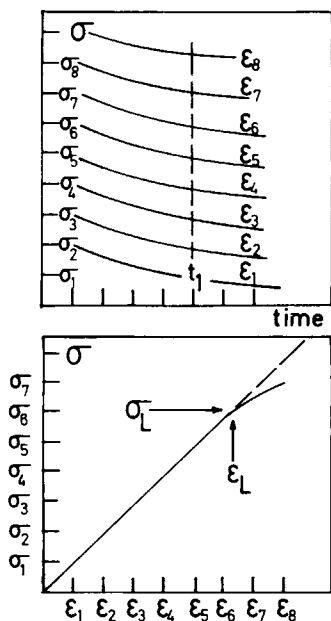


Fig. 1. Construction of an isochronous diagram at time t_1 from stress relaxation data.

EXPERIMENTAL

The recipes for the vulcanizates studied are shown in Table I. SAF is a superabrasion furnace black, which is a reinforcing carbon black. It has a higher specific area than the nonreinforcing Thermax MT black. Material A is unfilled. The crosslinking agent used was tetramethylthiuram disulfide (TMTD). The network obtained after vulcanization with TMTD contains, according to Brydson,⁸ mono- and disulfidic crosslinks, which are known to resist degradation and rearrangement. The relaxation experiments were made in air at 298 K with the thermostated relaxometer shown in Figure 2. The deformation was imposed by the movable slide and the load was measured by the load cell which was connected over an electronic strain-gauge bridge to a recorder. Two markings were made on the samples, and the elongation was determined by a cathetometer.

The crosslink density was found by swelling measurements to be approximately identical for materials A–C. Strips 10 cm long, 3 mm wide, and 1 mm thick were used. These were made by Skega AB, Ersmark, Sweden. Since the humidity can influence the relaxation rate, as reported by Derham,⁹ this was

TABLE I
Recipes of Materials Studied^a

Material	A	B	C
Natural rubber	100	100	100
N 110 (SAF)		50	
Thermax MT			50
Stearic acid	1	1	1
ZnO	3	3	3
TMTD	8	8	8

^a Curing temperature: 430 K; curing time: 16 min. Units: phr.

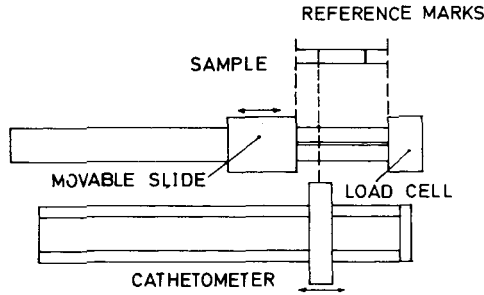


Fig. 2. Relaxometer with cathetometer.

checked with a hygrometer. During the measurements, the humidity varied within fairly narrow limits. In accordance with Yannas,³ the strain measure $1/3(\lambda^2 - \lambda^{-1})$ was used, where λ is the extension. The stress was calculated by dividing the measured force by the actual cross-sectional area.

The measurements for the determination of ϵ_L were made on specimens which had not been previously strained.

In the second part of the investigation, the influence of prestrain was studied. The specimen was stretched to the desired prestrain for 60 s and then unloaded for 15 min before being subjected to a further stress to enable data to be obtained so that the isochrone at 100 s could be constructed. This process was repeated in steps of 5% until a prestrain of 25% was reached.

RESULTS

Isochronous diagrams were drawn from stress relaxation data recorded at 100 s, as illustrated in Figure 3 for material A, for which the limiting strain ϵ_L is 14%. In Figure 4, ϵ_L for the filled materials B and C was found to be 7 and 3.5%, respectively. The results from the prestrain experiments are shown in Figure 5; ϵ_L was found to increase with increasing prestrain for all materials.

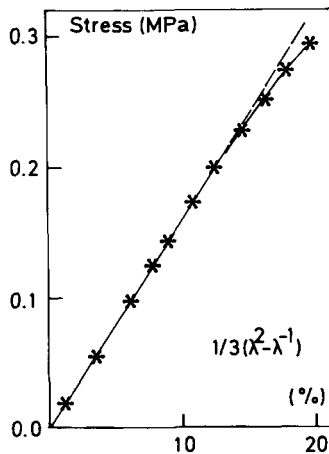


Fig. 3. Isochrone for material A (no filler) at 100 s. Limiting strain = 14%.

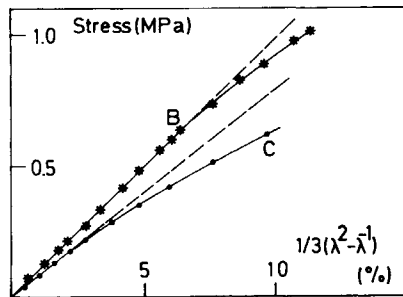


Fig. 4. Isochrones for materials B (SAF) and C (Thermax MT) at 100 s. Limiting strains: 7% (material B), 3.5% (material C).

DISCUSSION

The fact that ϵ_L is lower for the filled vulcanizates (B and C) than for the unfilled material (A) can probably be explained by the concept of strain amplification.¹⁰ The filler will be essentially undeformed, and the strain (macroscopic strain) is less than the strain in the rubber phase. The ϵ_L is lowest for the vulcanizate with the nonreinforcing filler Thermax MT.

The nature of the transition from approximately linear to nonlinear viscoelastic behavior is difficult to explain. For glassy polymers, it has been suggested that it is caused by stress-activated changes in the nature of the deformation mechanisms. In the rubbery state, the transition is probably mainly associated with additional effects such as constraints on large conformational movements being set up as the macroscopic strain increases.

The deviation from linearity is toward the strain axis, however, and this means that the material becomes softer above the transition. This contradicts the idea of the constraints. If the results are discussed in terms of a distribution of ordered suprastructures, the deviation from linearity toward the strain axis can be explained as resulting from the successive breakdown of such stiffer suprastructures, as has been discussed by, for instance, Blockland and Prins¹¹ and Bartenev and Lyalina.^{6,7,12}

Prestrains lower than the limiting strain ϵ_L for the unstrained material will

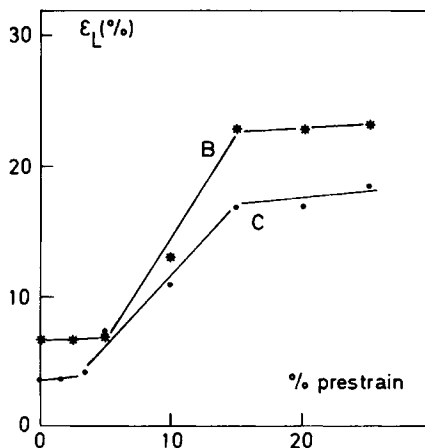


Fig. 5. Dependence of limiting strain on prestrain.

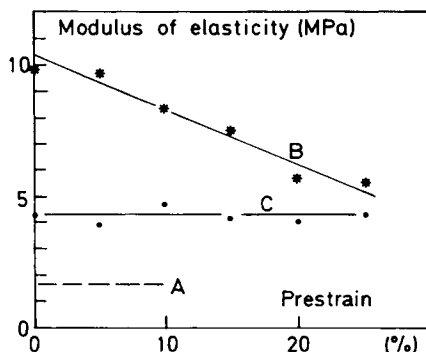


Fig. 6. Dependence of modulus of elasticity on prestrain. Material B contains the reinforcing filler SAF, and material C contains the nonreinforcing filler Thermax MT. Material A represents the unfilled material.

not change this value. When, however, the prestrain is higher than the initial ϵ_L , a higher ϵ_L will subsequently be obtained. This is observed for materials B and C. The same tendency holds also for material A, when the prestrain exceeds 14%.

A modulus of elasticity-prestrain relationship derived from isochrones constructed from data obtained at different prestrains is shown in Figure 6. The modulus for material C is evidently independent of the prestrain. This must mean that Thermax MT mainly acts hydrodynamically. For material B, the modulus decreases linearly with increasing prestrain. This decrease is probably equivalent to the strong dependence of the dynamic modulus on amplitude earlier reported for filled rubbers by Payne.¹³ The difference between the curves representing materials B and C reflects the reinforcing effect of SAF, and the difference between the curves representing materials C and A reflects the hydrodynamic effect of the filler.

CONCLUSIONS

Transition from approximately linear to nonlinear viscoelastic behavior for natural rubbers occurs at lower strains when the carbon black content is increased.

At a given filler concentration, the limiting strain is highest for the most reinforcing carbon black.

Prestraining increases the limiting strain.

The reinforcing effect of carbon black can be estimated by determining the extent to which prestraining influences the linear viscoelastic properties of vulcanizates.

The authors gratefully acknowledge the support from the Swedish Board for Technical Development and from the Swedish rubber industry. We also wish to thank Professor Bengt Rånby for continual support and interest during this work.

References

1. I. V. Yannas and A. C. Lunn, *J. Macromol. Sci.-Phys.*, **B4**(3), 603 (1970).
2. I. V. Yannas, N-H. Sung, and A. C. Lunn, *J. Macromol. Sci.-Phys.*, **B5**(3), 487 (1971).
3. I. V. Yannas, *J. Macromol. Sci.-Phys.*, **B6**(1), 91 (1972).
4. I. V. Yannas, *J. Polym. Sci., Macromol. Rev.*, **9**, 163 (1974).

5. A. V. Tobolsky, *Properties and Structure of Polymers*, Wiley, New York, 1960.
6. G. M. Bartenev and N. M. Lyalina, *Plaste Kautschuk*, **16**, 901 (1969).
7. G. M. Bartenev and N. M. Lyalina, *Polym. Sci. USSR*, **12**, 420 (1970).
8. J. A. Brydson, *Rubber Chemistry*, Applied Science Publishers, London, 1978.
9. C. J. Derham, *J. Polym. Sci. Phys.*, **13**, 1855 (1975).
10. M. Shen, in *Science and Technology of Rubbers*, F. R. Eirich, Ed., Academic Press, New York, 1978, Chap. 4.
11. R. Blockland and W. Prins, *J. Polym. Sci.*, **7**, 1595 (1969).
12. G. M. Bartenev and N. M. Lyalina, *Plaste Kautschuk*, **24**, 741 (1977).
13. A. R. Payne, Dynamic Properties of Filler-Loaded Rubbers, in G. Kraus, Ed., *Reinforcement of Elastomers*, Interscience, New York, 1965, Chap. 3.

Received February 5, 1981

Accepted April 27, 1981