

Stress Softening of Reinforced Vulcanizates by Swelling in Solvents

A model, by means of which it is possible to describe the strain-stress behavior of carbon black-reinforced elastomers, has been established by Rigbi¹ based on a qualitative description by Dannenberg.² The model also appears to describe adequately the phenomenon of stress softening and, after suitable modification, the behavior at high rates of strain.³

Careful inspection of the model indicates that a phenomenon similar to stress softening should also appear following swelling of the loaded vulcanizates in solvents. In the original model, stress softening is postulated to arise as the result of the movement of a crosslink relative to a carbon-black agglomerate, this being the microscale result of an overall strain; the stress developed in the molecular chain then results in a net increase in the chain length and, consequently, a fall in modulus. Similar behavior must also appear in a swollen vulcanizate, in which the crosslinks and agglomerates move affinely in three dimensions rather than uniaxially.

However, swelling of reinforced vulcanizates has not, in the past, been observed to produce stress softening. When such studies were made, a hardening was almost always noted due to the removal of plasticizing oils or of curative adjuncts such as fatty acids.

This note gives details of the experiments carried out in order to detect stress softening and the theoretical reasoning behind them.

Theory

As described earlier,¹ stress softening and its recovery are highly temperature-sensitive processes which, presumably, cease completely at the glass transition temperature. However, at temperatures low enough even if they are well above T_g , these processes must be extremely slow, since it has been shown⁴ that at 0°C, the recovery from stress softening virtually disappears in compounds for which T_g is of the order of -40°C. In the case of vulcanizates swollen by means of nonfreezing solvents, the glass transition is considerably reduced, and, if the time-temperature shift applies to stress softening, recovery (as appears likely from the work of Kraus et al.⁵), may still be an important factor at 0°C. It was therefore proposed to prevent recovery, if softening did occur, by means of one of the following methods: (1) reduction of the temperature to the lowest practical level during drying out of the solvent; (2) removal of the swelling solvent by means of immersion in a low-viscosity nonsolvent; (3) combination of the above two methods.

Experimental

In order to obtain maximum swelling and presumably greatest stress softening,* the swelling solvent selected was chloroform with methanol as the nonsolvent. The temperature obtained in the freezer compartment of a laboratory refrigerator, -8°C, was chosen for the low temperature, as it was not considered desirable to use more sophisticated equipment.

Strips, 1/4 in. wide, of a polybutadiene/50 ISAF vulcanizate, containing no softening oils, were extracted by immersion in chloroform, and dried at room temperature. These were then subjected to various swelling and deswelling treatments as follows: group 1, as received after extraction (control group); group 2, swollen in chloroform at room temperature, dried at room temperature overnight; group 3, swollen in chloroform and deswollen in methanol, both at room temperature, followed by vacuum drying at room temperature for 1 hr; group 4, swollen in chloroform at room temperature, deswollen in methanol at -8°C, vacuum-dried at room temperature for 1 hr; group 5, swollen at -8°C, dried at room temperature overnight; group 6, swollen at -8°C, deswollen

* It must be obvious that this is not a truly descriptive term for the process. However, it is retained here because of its acceptance in other papers on the subject.

in methanol at room temperature, vacuum-dried for 1 hr at room temperature; group 7, swollen at -8°C , deswollen in methanol at -8°C , vacuum dried for 1 hr at room temperature; group 8, immersed for 24 hr in methanol at room temperature, vacuum-dried for 1 hr at room temperature; group 9, immersed for 24 hr in methanol at -8°C , vacuum-dried for 1 hr at room temperature.

Three strips of each group were tested in an Instron tester at cross-head speed of 100 cm/min with a gage length of 10 cm, and the stress readings were compared by averaging the three values obtained for each group.

A number of specimens were also weighed: chloroform absorptions at room temperature and -8°C were obtained, and it was seen that weight changes on drying were minimal, reaching 0.4% in two cases only. Specimens were therefore presumed to be solvent-free when tested on the Instron.

Results and Discussion

The absorption of chloroform was measured to be 256% by weight at room temperature and 209% at -8°C . These figures correspond to volume swells of 270 and 220%, or linear "swell" of 55 and 47%, respectively.

The averaged Instron traces for groups 1, 2, 8 and 9 are virtually indistinguishable, as shown on Figure 1, indicating that drying the swollen vulcanizate at room tempera-

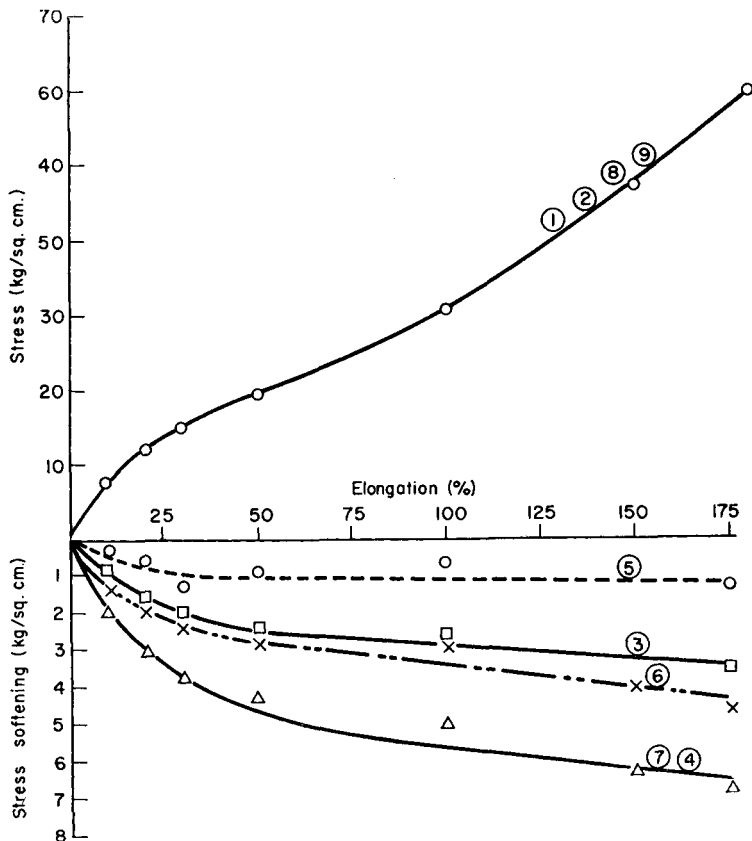


Fig. 1. Stress softening of a 50 ISAF/polybutadiene vulcanizate after swelling in chloroform. Numbers refer to deswelling treatments described in text.

ture eliminated the effects of stress softening if any had indeed been induced by the swelling process. The effects of the treatments described for the other groups is shown as stress softening, (i.e., differences in the values of the modulus at various elongations) on the same graph. The following deductions can now be made. (a) Swelling in chloroform at -8° and drying at room temperature involves little net stress softening. The scatter at this low level makes it doubtful whether any softening did actually occur. (b) Deswelling in methanol at room temperature, a process which does not require more than 3 hr, shows more stress softening. (c) Deswelling in methanol at room temperature following swelling at -8°C shows stress softening to an even greater extent. It is probable that the lower temperature of the specimen may have been responsible for the preservation of stress softening to a greater extent than simple deswelling, particularly considering that the induced softening must have been smaller due to the lower swell at -8°C . (d) Deswelling at -8°C of samples swollen at room temperature and -8°C results in residual stress softening almost identical to that in (c).

It may therefore be concluded that swelling induces stress softening, but that ordinary methods of drying allow complete recovery. However, rapid deswelling in a nonsolvent, particularly at low temperature, reduces the recovery of stress softening. These conclusions support the model proposed for reinforcement of elastomers by carbon black¹ and the kinetic mechanism developed for it.

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Z. RIGBI

Department of Mechanics
Technion—Israel Institute of Technology
Haifa, Israel

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