

Structural changes in filled elastomers subjected to stretching and recovery of their properties in thermostating

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Abstract

An experimental study showed that the growth of damage in rubbers subjected to repeated loading was not the only reason for hysteresis losses. The viscoelastic properties of elastomeric material also contributed to the hysteresis losses. Owing to these properties, the material is capable of partial or complete recovery of its mechanical properties after a long while or during heat treatment.

Numerous experiments on cyclic high-amplitude loading of rubbers have shown substantial hysteresis losses to occur during the first loading cycle; in the subsequent cycles, the losses decrease and the material becomes less stiff [1, 2]. This phenomenon is known as the Mullins effect and is attributed to a growth in damage of rubbers [3, 4]. The cause of these losses may also be the viscoelastic properties of the elastomer. The objective of this investigation was to study the viscoelastic properties in filled elastomers.

We performed experiments in which a specimen was subjected to cyclic stretching until the stabilization of hysteresis losses was reached. Then the specimen was held at a fixed temperature. Depending on the holding temperature, the mechanical properties of the rubber were recovered partially or completely.

The elastomer used in the study had a carbon-black volume fraction of 50% and a breaking extension of 250%.

Specimens were prepared in the form of a ring of 50 mm outer diameter, 4 mm width, and 2 mm thickness. The ring was put on round grips designed for this purpose and stretched. The merit of this shape of specimens was that they could not slip out of the grip fixtures at large strains or be damaged by clamping.

Special measures were taken (labels were attached) to control the base distance during the removal of the sample from the grips and its thermostating for a given period of time.

Specimens prepared for testing were preliminarily annealed at 100°C for 72 h to stabilize their properties and to remove stresses induced during their preparation and storage. The specimens were stretched at 20°C with a speed of 100 %/min in a 2167 P-50 tensile-testing machine.

Experiments were performed on several specimens of identical geometrical dimensions, which were subjected to identical thermal treatment prior to testing. At the beginning of testing, the specimens were cyclically loaded to the same deformation. The plots of cyclic stretching were identical for all the specimens. After preconditioning the specimens were thermostatted for different periods of time. Note that the recovery of their properties after long-term thermostating was complete.

Figure 1a presents the stress-strain plots under cyclic loading of a specimen to an extension ratio of 50% and the plots for specimens held at 100°C for 1 and 72 h.

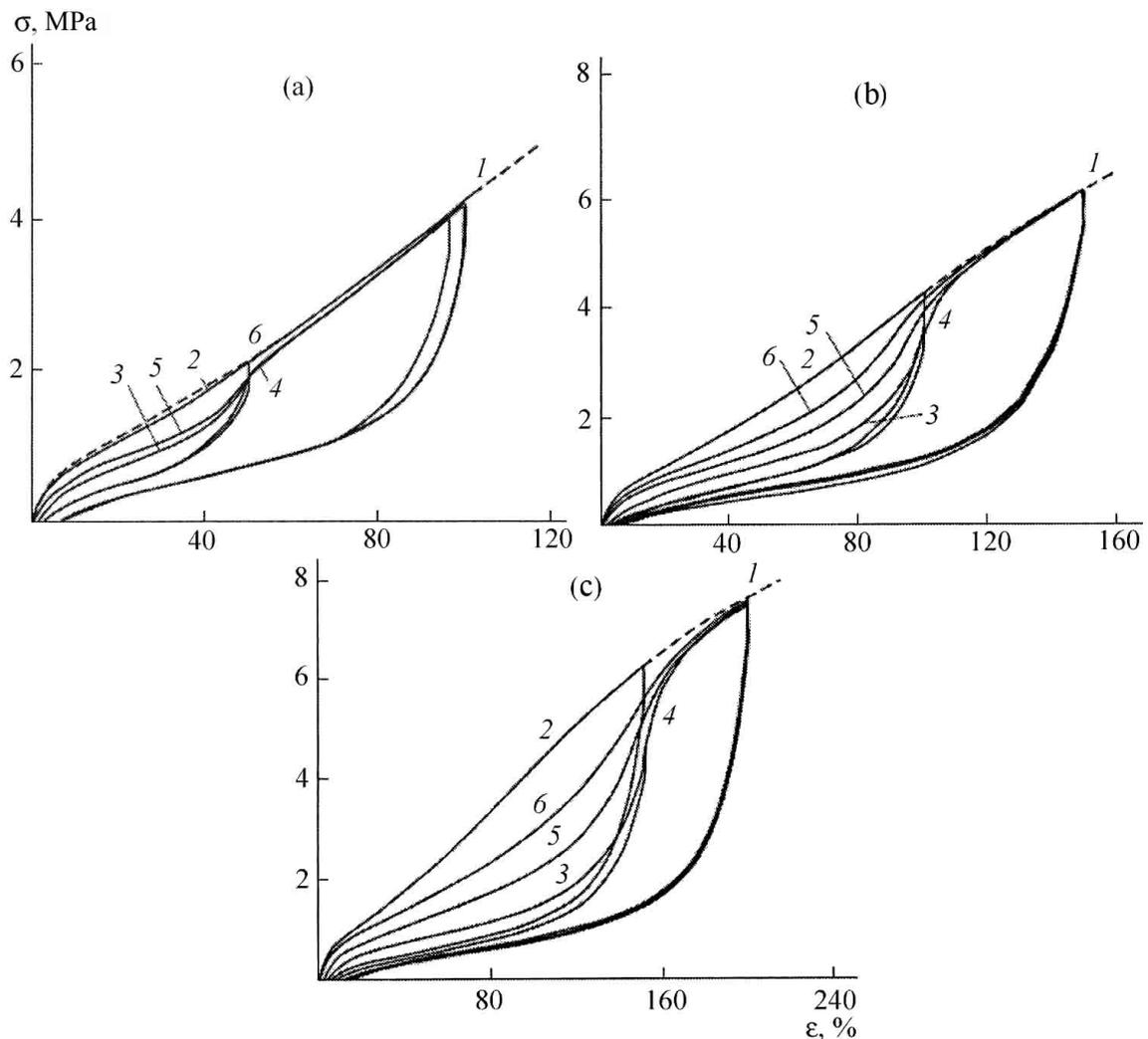


Figure 1: Tensile loading-unloading curves of thermo-statted specimens. Specimen preconditioning at an extension ratio of (a) 50, (b) 100, and (c) 150%: (1) single-stretching curve, (2) first loading of the virgin specimen, (3) the last cycle of specimen loading during conditioning, (4) immediate (without thermo-stating) stretching of the specimen to an extension ratio greater than the preconditioning extension, (5) stretching of the preconditioned specimen after thermostating for 1 h, and (6) the same after 72-h thermostating.

Figures 1b and 1c show similar plots. In these cases, the specimen was preliminarily subjected to cyclic stretching to 100 and 150%. The specimens thus aged were thermostatted for 1 and 72 h and then stretched to a higher extension ratio.

From Fig. 1, it is seen that the specimens thermostatted for 1 h partially recovered their mechanical properties.

Thermostating for a long period of time (to 72 h) leads to the maximum recovery of properties. At a low preliminary extension level (to 50% in the given case), the specimen completely recovers its properties. However, if a specimen is conditioned at a higher extension ratio, there is no complete recovery of the properties.

It may be assumed that there are two possible ways of evolution of the structure of material — free and forced. The forced evolution of the material structure manifests itself

when the stretching of a specimen causes the tightening of loops in molecular chains at the molecular level, the slipping of chains, and their debonding from filler particles. This evolution occurs under an external load. In turn, unloading leads to the loosening of loops and the crawling of chains over or their adhering to inclusions. Under these conditions, the kinetic energy of motion of polymer chain units is insufficient for the reverse process of recovery to occur at the same rate as upon loading.

The loops tied to very tight knots take a very long time to disentangle and the formation of the initial polymer-network morphology is very slow. Let us call this the free evolution of the material structure. The softening of the material strongly depends on the volume fraction of filler and is substantially less dependent on the elastomer-crosslink density [5]. After a long rest (tens or even hundreds of days) at room temperature, the initial properties of rubbers may be recovered [6] (Fig. 2). The same takes place after thermostating the specimens for a certain time — 3 days in our experiments. This suggests that the defects induced are either healed or the softening effect has a nature other than damaging, for example, thixotropic (as a consequence of desorption of taut chains from the filler surface [7], phase transition in the elastomer matrix near filler particles [8], or slippage of polymer chains on the filler surface [9]).

Fukahori [10] reported experimental data suggesting that filled elastomers have a much more complex structure than was anticipated. The complex structure has a softening nature due to different causes associated with both viscoelastic mechanisms (thixotropic properties) and damage buildup.

Figure 2 depicts a tensile stress-strain curve after resting a specimen at room temperature for 256 days. These data confirm that the recovery of the elastomer properties takes place at room temperature as well. The process is due to the thermal motion of molecules, and this takes time. Heating only accelerates the thixotropic processes.

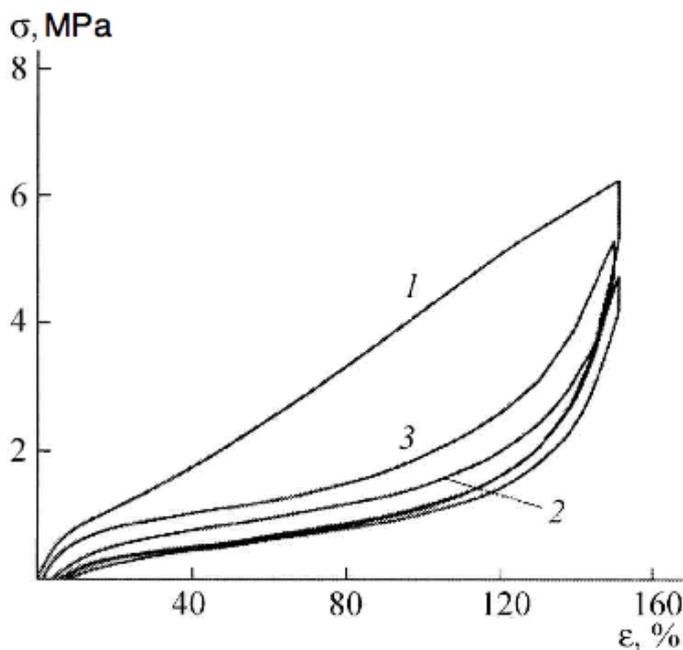


Figure 2: Recovery of the mechanical properties after 256 days of rest: (1) first stretching of the specimen to 150%, (2) the last cycle of stretching the specimen during its conditioning, and (3) specimen stretching after resting for 256 days.

From the data presented in Figs. 1b and 1c, it is seen that, at large extension ratios (more than 50% in our case), other processes that are presumably due to damage buildup occur in the elastomer along with the changes related to the viscoelastic properties. The greater the extension ratio during the preliminary cycling, the greater the amount of damage that is not healed with time (upon thermostating).

What is noteworthy in Fig. 1 is that the material “remembers” its ultimate strain. When the specimens are stretched to an extension ratio that is higher than the one at which a specimen was conditioned, the stress-strain curve very rapidly reaches the level of the single stretching of the virgin specimen. This phenomenon is easy to explain in terms of both viscoelastic properties and damage buildup. However, the complete recovery of the initial properties of the specimen stretched to an extension ratio of more than 50% does not take place even after long-term thermostating. The stress-strain curve after thermostating lies below the first-stretching curve (Figs. 1b, 1c). This indicates that the changes associated with the structure recovery are not accomplished to the full extent at large deformations and the damage buildup process occurs simultaneously with thixotropic changes.

The results obtained in these experiments show that, in addition to damage buildup during deformation of rubbers, a considerable contribution to hysteresis losses is made by the viscoelastic properties of the elastomer matrix.

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