Volume Changes in Filled Rubber Under Uniaxial Cyclic Loading

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Styrene-butadiene rubber, neat and filled with different silica content was investigated under uniaxial cyclic loading under a constant crosshead speed, with increasing deformation amplitude in subsequent loading cycles. Rubber was investigated in order to evaluate the reversibility of structure rearrangements, occurring in rubber when subjected to cyclic loading.

Volume uniformly increases with growing strain and shows hysteresis at unloading. After complete unloading, no residual strain changes are observed. These data are in good conformity with the data of density measurements, which were made on specimens before and after the tests. By correlating data, obtained from volume changes and kinetics of hysteresis losses there were made assumptions on deformation mechanisms at different elongations.

Deformational mechanisms, responsible for volume changes in rubber are reversible. Volume changes in specimen occur due to voids formation caused by filler microstructure breakage, rubber chains disentanglement, spaces between rubber macromolecular chains shrinkage, and chain slippage under higher elongations. Voids formation and deformation of rubber macromolecular chain reaches equilibrium state after certain elongation.

Keywords: rubber, volume changes, cyclic loading.

INTRODUCTION

Rubbers are widely used as industrial materials, especially in tire industry; its fortification with fillers is a common practice. Filler addition and strain application leads to rubber hardening, which happens due to chemical and physical interaction between filler particles and rubber macromolecular chains, and particle-particle interactions, thus occurs on different levels of structure. In filled rubber, fortification effect usually is divided into several stages: (1) fortification due to incorporation of rigid inclusions into rubber structure, (2) filler-rubber formed bonds and (3) filler-filler formed bonds of filler formed microstructure. Depending on bond type between filler surface and elastomer network, different processes can be dominant in fortification, such as: molecular slippage or molecular segments rearrangement and orientation, particle displacement and failure of filler formed network and other processes [1]. Softening is mainly associated with properties of rubber macromolecular network as well as with features of particle-rubber interactions.

Filler, in addition to improving rubber properties may lead to additional effects emerge, such as Mullins effect or softening. The Mullins effect is still under investigation due to its complex nature. It can be observed under cyclic loading experiments with increasing strain amplitude [2, 3]. Softening can be observed in both, filled and neat rubbers.

The hysteresis losses are quantitative feature of the softening. By analyzing kinetics of changes hysteresis losses with growing strain for elastomer, it is possible to evaluate contribution of different mechanisms of softening at different stages of deformation, and, thus, make some conclusions on processes that cause volume changes of rubber [4].

The main cause of energy loss associated with rolling resistance is hysteresis, it is mainly attributed to the viscoelastic characteristics of the rubber. Part of energy, spent on elastomer deformation, is dissipated on viscous resistance of molecular rearrangement and overcome of structure failure. Energy dissipation mechanisms in rubber are mainly associated with two reasons.

The first reason is inner viscosity of rubber, which occurs when molecular chains change their conformations and slippage of segments begins. Inner viscosity resists to molecular chain rearrangement and is associated with segmental moving ability. Small deformations are associated with deformation of unmovable segments (straightening), and corresponding dissipated energy contribution is low. Segmental viscosity increases with increase of deformation, thus contribution of dissipated energy increases.

The second reason of energy dissipation is failure of filled elastomer structure, which is a two-phase system. Rigid filler particles strengthen elastomers because of formation of long filler formed chains and by gluing to adjacent rubber molecules. All these bonds partly failure at elongation: filler formed chains – at relatively small strains, and filler-rubber bonds – at larger strains. Energy, spent on deformation of filled elastomer thus partly dissipates in these irreversible processes [5].

Under service conditions, rubber usually exhibits repeated cycles of deformation. These conditions may lead to irreversible structure reorganizations, which can be observed as changes in volume or density. Thus, by investigating these material properties, assumptions on reversibility of processes, occurring in rubber during deformations, can be made.

Many studies, such as [4, 6 – 12] are devoted to hysteresis losses and softening in elastomers investigation, but, the number of studies devoted to volume changes investigation is much less. Thus, the aim of the study is to estimate the contribution of deformation-recovery

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mechanisms into rubber deformational behaviour by studying volume changes and to evaluate their reversibility; to review rubber performance under cyclic loading experiment; to correlate data, obtained from hysteresis losses determination and volume changes investigation.

MATERIALS AND EXPERIMENTAL DETAILS

Material under study is styrene-butadiene rubber, neat and filled with different volume content of silica filler: $f = 9$, 14 and 21 volume %. Dumbbell like specimens with thickness of 1.2 mm to 2.0 mm depending on the compound were used.

Uniaxial tension tests were carried out using Zwick 2.5 testing machine with a load cell of 2.5 kN. The operative part from specimens had a length of 20 mm and width of 5 mm.

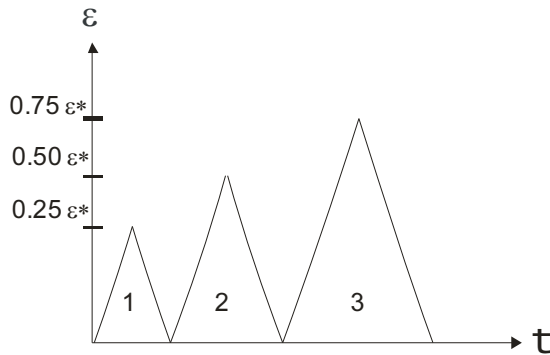Three loading-unloading cycles were applied to each specimen, according to the scheme shown in Fig. 1.

Fig. 1. Scheme of applied loading cycles, subsequent cycles are numbered

Maximum strain level in subsequent cycles corresponded to 0.25, 0.5 and 0.75 from the strain at failure. Specimens were stretched and retracted at a constant crosshead speed of 50 mm/min, which corresponds to a nominal strain rate of 0.033 s^{-1}. Strain at failure was determined in standard uniaxial tension tests with the same strain rate. The ultimate characteristics are given in Table 1. Specimens were preloaded up to 0.5 N for avoidance of their contortion. All tests were performed under room conditions with average of 22 °C.

Table 1. Average ultimate characteristics of studied styrene-butadiene rubber

Filler volume content f, %	Stress at failure σ^*, MPa	Strain at failure ε^*, %
0	1.0 ±0.05	252 (±16)
9	4.6 ±0.5	514 (±37)
14	18.0 ±1.6	866 (±45)
21	21.4 ±1.4	711 (±33)

Strains were measured by a photo method. White markers were marked on operative part of specimens and their displacement along time was measured by a high resolution photo camera. Relative displacement, which is proportional to the nominal strain, was determined using special software, developed in Institute of Polymer

Mechanics [13], by treatment of photo images obtained during tests.

Relative volume changes $\dfrac{\Delta V}{V_0}$ were calculated using following formula:

$$\frac{\Delta V}{V_0} = (1+\varepsilon_1)(1+\varepsilon_2)(1+\varepsilon_3)-1 =$$
$$= (1+\varepsilon_1)(1+\varepsilon_2)^2 - 1 \tag{1}$$

where ε_1, ε_2, ε_3 is specimen strain under stress, V_0 is the specimen volume before stress application, ΔV is the specimen volume changes under stress. In this notation, number indicates direction of measurement: ε_1 is the longitudinal strain, ε_2, ε_3 are the transversal strains. ε_2 and ε_3 are assumed equal because of incompressibility of rubber.

Hysteresis losses H were calculated by the ratio of areas under loading and unloading curves.

$$H = \frac{S_{load} - S_{unload}}{S_{load}} = 1 - \frac{S_{unload}}{S_{load}}, \tag{2}$$

where S_{load} is an area under loading curve, S_{unload} is the area under unloading curve in cyclic loading experiment. Kinetics of the hysteresis losses was determined by evaluation of the corresponding areas under loading and unloading curves at different strain values.

Density measurements were performed on Mettler Toledo balances by hydrostatic weighting. Specimen density was measured in acetone; before and after cyclic loading tests. Density of specimens was also calculated using the rule of mixture:

$$\rho_{composite} = \rho_{silica} \cdot f + \rho_{rubber}(1-f), \tag{3}$$

where density of silica $\rho_{silica} = 2$ g/cm^3 and density of the neat rubber $\rho_{rubber} = 0.97$ g/cm^3.

RESULTS AND DISCUSSION

Typical stress-strain curves, obtained in uniaxial cyclic loading experiment for rubber with $f = 21$ % are shown in Fig. 2. As seen from the figure, under repeated tensile strain silica filled rubber exhibits a reduction in stress. In following cycles, significant softening occurs after strain exceeds maximal strain value of previous cycle, difference in stress between loading and unloading curves increases significantly in the 2nd and the 3rd cycles. Loading curves of subsequent cycles follow the same path as the monotonous stress-strain curve, obtained in uniaxial test. The amount of softening increases with the maximum stretch. After reaching the stress-strain test curve, loading curves start to overlap it; this means, rubber rigidness increases. Unloading curves overlap in more complicated manner: loading curve of the 2nd cycle repeat unloading curve of the 1st cycle, while loading curve of the 3rd cycle repeats the path of unloading curve in the 2nd cycle. Residual strain is noticeable after the first stress-strain cycle and no significant changes appear in subsequent cycles. Stress-strain curves for neat rubber are shown in Fig. 3. In this case, loading-unloading curves coincide with stress-strain test curve. Rubber ability to exhibit deformation decreases, residual strain is negligible.
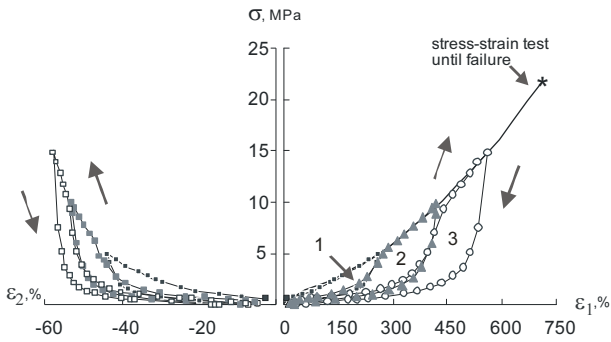
Fig. 2. Stress-strain curves for rubber with 21 % of silica filler in cyclic test and stress-strain test until failure. Numbers indicate loading-unloading cycle (1 – first cycle; 2 – second cycle; 3 – third cycle)
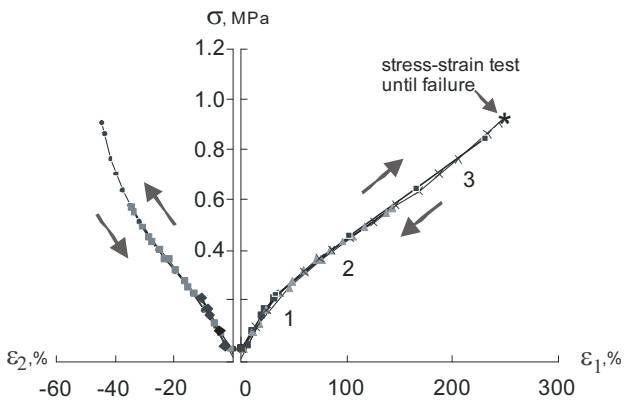

Fig. 3. Stress-strain curves for neat rubber in cyclic test and stress-strain test until failure. Numbers indicate loading-unloading cycle

Fig. 4. Volume changes for rubber with 21 % silica filler amount. Numbers indicate loading-unloading cycle

Fig. 5. Volume changes for neat rubber. Numbers indicate loading-unloading cycle

Rubber deformability is mainly caused by capability of rubber chains for reversible deformations, which forms a network because of crosslinks [275]. Filled rubber structure includes additional bonds between macromolecules of rubber and the filler, thus rubber can exhibit larger strains. Filler inclusion in rubber microstructure leads to rubber hardening. This happens because filler particles form a microstructure which by itself consists of particle formed agglomerates and chains, which link up agglomerates. Under stress application, filler formed microstructure fails gradually; this process begins under small elongations and continues with strain increase, causing softening of rubber, thus, softening of neat rubber is not essential.

Strain dependences of volume changes for rubber with $f = 21$ % are shown on Fig. 4 as an example. As seen from Fig. 4 and Fig. 5, increase in strain leads to an increse of area of volume changes curves loop. After threspassing certain elongations, volume changes tend to some equilibrium, which is observed as a decrease of slope of the loop. After removing stress, volume changes tend to zero, and are fully recoverable.

Volume changes are reversible for all rubber compositions (Fig. 6), unloading curves in all cycles return to its initial point. This confirms the recoverability of processes, causing rubber deformation.

Under low strains, slope of volume changes curves is similar for all rubber compositions. In this stage of elongation, rubber deformation is caused by elasticity of rubber macromolecular chains, breakage of filler formed network occurs (in filled rubber).
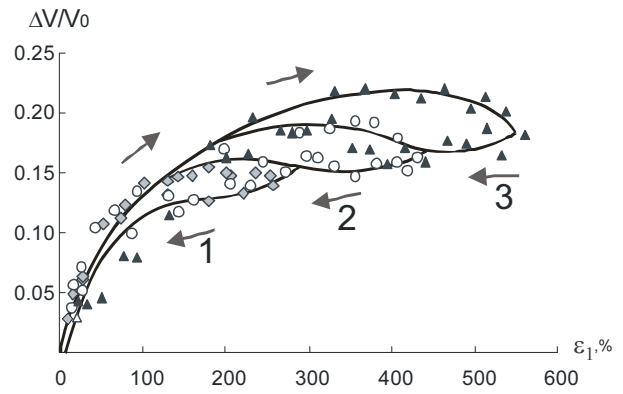
Under larger strains, loop between loading and unloading curves is observed. For rubbers without filler, loading and unloading curves overlay. Increase in loop area occurs due to filler-rubber bonds breakages, which partly recover after strain removal. At unloading, part of broken bonds recovers from breakage, but re-aggregated bonds are weaker than undamaged ones, thus, rubber softening is observed. The higher is filler content, the higher is its contribution to rubber deformation. For neat rubber, damage mechanisms caused by filler inclusions do not contribute to volume changes. These effects are recoverable; after repeated loading volume changes practically return to its initial values as seen on the figure. At larger strains, volume changes tend to certain equilibrium between bonds breakage, voids formation and lateral contraction. This is observed, as decrease in slope of volume changes curve in Fig. 5.

Kinetics of hysteresis losses is shown in Fig. 7. As seen from the figure, hysteresis losses curves path is not monotonic, i.e. after passing maxima point of kinetics of hysteresis losses in prevous cycles, increase in losses values is sheared to lager strains. In the first cycle, slope of the hysteresis losses curve changes, but no maxima can be noticeable. In the 2nd and the 3rd cycles, after increase in hysteresis losses, its values decrease. After passing the first maxima point, hysteresis losses decrease until second maxima is observed. After repeated loading, material becomes more flexible and second maxima is shifted to larger strains, as seen on Fig. 7.

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At small elongations, rubber elasticity is conditioned with rubber macromolecular chain disentanglement. At this stage, filler formed network breakage is intensive, so contribution to overall rubber structure breakage due to deformation comes mainly from this process, and increase in hysteresis is observed Fig. 7. Further increase in strain leads to gradual filler microstructure failure, so contribution of this process into rubber structure destruction lessens, rubber deformation occurs due to macromolecular chain disentanglement and elongation. Contribution of both of these processes to rubber failure is comparable, decrease in hysteresis losses values and in slippage of curve is observed.
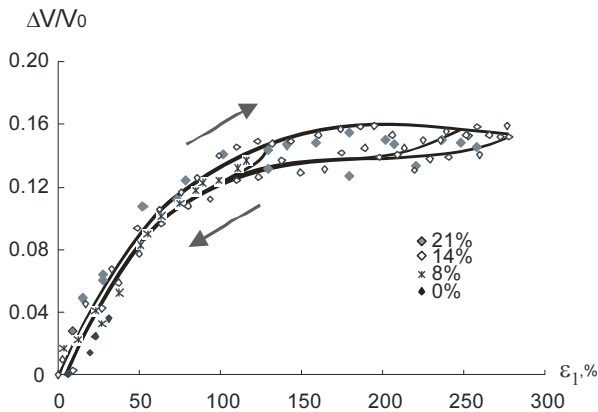

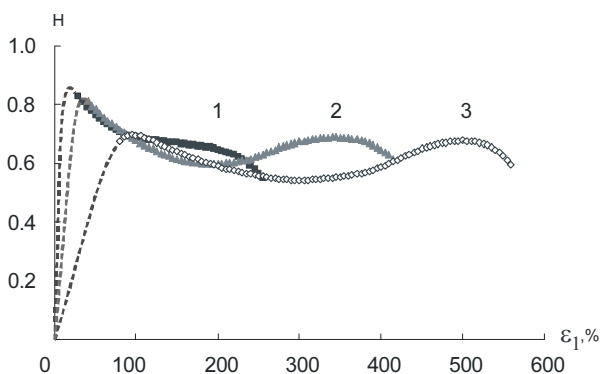**Fig. 6.** First cycle of volume changes for rubbers with different filler amount

Fig. 7. Dependency of hysteresis losses on deformation for rubber with 21 % silica filler amount. Numbers indicate loading-unloading cycle

At large strains, filler-filler and filler rubber bonds breakage takes place. Under these deformations, stiffness of rubber macromolecular chains increase, chains slippage and breakage begins. All these processes cause rubber structure failure, thus hysteresis losses values increase, second maxima occurs Fig. 7. Further strain increase leads to specimen cross-section area decrease, as a result, chains press to each other. Rigid chains, conformed closer to each other, cannot change their orientation, thus slippage and breakage of chains begins, which leads to increase of hysteresis losses.

Density of rubber as function of silica volume content is shown in Fig. 8. Results show no significant changes in rubber density before and after tests. Density increases with growing amount of filler. The rule of mixture linearly fits the experimental data. As it was mentioned above,

recoverability of structural reorganizations in rubber can be confirmed by reversibility of volume changes. Similarly, no residual changes were observed in density values after cyclic loading application; results obtained from both experiments are in good correlation.
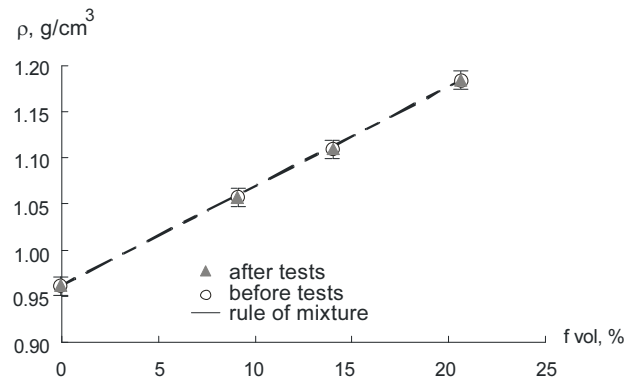

Fig. 8. Density dependence on filler content

To compare hysteresis losses and volume changes on similar stages of elongation, one can summon, that under low and medium low strains rubber macromolecular chains are elastic and do not resist structural reorganizations when subjected to elongations. On this stage, volume changes occur because of the rubber chain elasticity. Under larger strains, rubber chains loose their flexibility and become rigid. Relatively rigid chains hinder from conformations, slippage and rearrangement of chains begins, which leads to voids formation, and, thus, to increase of volume changes. Breakage of bonds between filler and rubber also occurs.

CONCLUSIONS

1. Volume uniformly increases with growing strain and shows hysteresis at unloading. After complete unloading, no residual changes are observed. This proves the fact that structural reorganizations under strain application in rubber are practically reversible. At identical elongations hysteresis between loading and unloading curves for rubbers with different silica content is similar. Increase in strain leads to increase of area of volume changes curves loop, while slope of loop decreases.
2. Density measurements show no significant changes in rubber density before and after tests. This proves the fact that rubber structure reorganization due to elongation is reversible. Data are in good correlation with results, obtained from volume changes.
3. Volume changes in specimen occur due to voids formation caused by filler microstructure breakage, rubber chains disentanglement, spaces between rubber macromolecular chains shrinkage, and chain slippage under higher elongations. After certain elongation, voids formation and rubber macromolecular chain deformation reaches equilibrium state; after stress removal volume changes in specimen are negligible. This confirms the fact that under repeated loading filler microstructure formed bonds and filler-rubber formed bonds gradually weaken and tend to some equilibrium, i. e. are capable to practically complete recovery.

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