

Experimental studies of rubbers filled by layered clay nanoparticles

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Abstract

It is known that one of the main and most common fillers of rubbers based on natural and synthetic caoutchoucs are carbon black (black soot) and oxides of zinc (white soot). Putting into an elastomer such substances can significantly improve its mechanical properties (especially strength and deformability). To date, these effects are well understood and can be said that this method of modifying the properties of the rubber reached the ceiling. Further progress requires a search for new nonconventional types of fillers. One of perspective directions is the use of various clay minerals.

The paper presents the results of experimental studies of elastomeric nanocomposites containing a new (for elastomers) type of filler — montmorillonite (MMT). This material, in particular processing, is capable to be dispersed nanoparticles of ultrafine flakes with a minimum thickness of up to 1 nm, that may form individual packs of parallel plates — tactoids.

Experimental studies conducted by a special technique, based on cyclic deformation of the sample with a stepwise variable amplitude of the deformations. Tests of this kind are used in when it is necessary to receive in one experiment comprehensive data about the viscoelastic and elastic-plastic material properties. It was found that the addition of clay nanofiller rubber contributes to significant dissipative losses increase, indicating that the development of viscoelastic processes in the composite during its deformation. Also, the relative softening of material (compared with pure vulcanizate) occurred at large cyclic strains (more than 3–4 times). And these effects were stronger than for fillers with a larger basal spacing.

1 Introduction

It is known that the most common fillers of rubbers based on natural and synthetic caoutchoucs are carbon black (black soot) and oxides of zinc ZnO (fumed silica). The input of these substances in the elastomer can significantly improve its mechanical properties (particularly strength and deformability). To date, these effects are well understood and can be said that this method of rubber modifying reached

the ceiling. Further progress requires a search for new and innovative types of fillers. One promising area is the use of various clay minerals. This allows naturally vary the shape and size of the filler particles, depending on the task (for example, montmorillonite provides ultrathin plates, palygorskite — nanoneedles, shungit — nanoglobules).

Nanostructured materials are characterized by an extremely high total filler surface area (by orders of magnitude higher than in conventional composites with a filler of micron sizes). Therefore properties of nanomaterials significantly more dependent on structural effects generated by interphase boundaries ("linked" polymer layers formed on the nanoparticle surfaces, interfacial adhesion, etc.).

The thickness of the interfacial layers is measured in nanometers, which is comparable with the length of the polymer molecular chains, and the physical properties of the layers can be significantly different from the rest of the matrix (due to the orientation impact the of the particles surface). For example, these can explain the fact, the addition of even small portions (usually 3–5% by weight) of silica nanofiller in the polymer can significantly improve its operational properties. Meanwhile, to get a similar effect in conventional composite materials the filler concentration should be at least an order of magnitude higher [1, 2].

Historically, the first mineral-filled nanocomposites were polyolefins (polyethylene, polypropylene, etc.) with a filler of layered clay minerals (montmorillonite) [3, 4]. Their first commercial application were different auxiliary parts in cars (Toyota, General Motors, Mitsubishi, Honda), as well as packaging for liquids (Alco SCI, Nanocor). These materials are characterized by good thermal insulation properties, low diffusion permeability, high thermal stability and resistance to combustion. Currently, one of the most promising applications of elastomers with mineral nanofillers are the vehicle tires. Rubbers with this kind of filler are cheaper and differ the raised wear resistance [5, 6].

2 The object of study

The main object of study were elastomeric nanocomposites containing relatively new (for elastomers) type of filler — montmorillonite (MMT). This material refers to a class of swellable clay minerals and at certain treatments able to break up into ultrafine flakes with a minimum thickness of up to 1 nm and the characteristic size from 30 nm to several microns. These nanoparticles can form separate bundles — tactoids of parallel plates (up to tens). Natural montmorillonite consists of randomly oriented tactoids.

MMT is a hydrophilic material, which makes it difficult to wetting by organic substances (usually hydrophobic). Therefore, the particles of montmorillonite are modified to improve the thermodynamic compatibility with the matrix polymer, i.e. the organophilic surface layers with the desired level of interaction with the polymer matrix are created. Various surface active agents (surfactants) are used for this purpose, including those organic. Surfactant layer thickness on the surface nanoplates can reach 1–2 nanometers. Clay minerals treated with organic modifiers, are also called organoclays.

Montmorillonite nanoparticles treated as surfactants by distearil dimethylammonium chloride were used at carrying out of mechanical experiments [7, 8, 9]. The characteristic average particle (tactoids) size D_{MMT} was about 65–70 nm, the average distance between the layers in tactoids (basal) $d_{MMT} = 2.9\text{--}3.0$ nm. MMT density equaled 1.8 g/cm^3 .

Materials for the study were provided by the Leibniz Institute of Polymer Research, Dresden, Germany (Leibniz-Institut für Polymerforschung).

Vulcanizates of natural rubber (NR), containing carbon black (CB) of N330 brand were used as a matrix. Concentration of other additives (mineral oil, white carbon (ZnO), sulfur, a vulcanization accelerator TBBS (N-tert-butyl-2-benzothiazolylsulfenamide)) was the same for all samples. Accordingly, the matters of their effect on changes in mechanical properties of the composite in this study were not considered.

Thus, the following materials were studied in the experiment (ψ_{CB} – CB mass concentration, ψ_{MMT} – mass concentration of MMT filler):

- 1) NR: pure natural rubber without filler (NR) as a basis for comparison;
- 2) NR-CB30: natural rubber, filled with 30 phr of CB ($\psi_{CB} = 21.2\%$ -wt.);
- 3) NR-CB30-MMT5: natural rubber, filled with 30 phr of CB ($\psi_{CB} = 21.2\%$ -wt.) and 5 phr of MMT ($\psi_{MMT} = 3.55\%$ -wt.).

3 Experiment

Experimental studies were carried out on the universal tensile testing machine Testometric FS100kN CT. The special technique was used, based on cyclic deformation of a sample with a variable step-by-step amplitude of deformations (and stops for relaxation when changing the direction of the load). Tests of this kind are usually used in the study of polymers, when it is required to obtain in one experiment complex data on the viscoelastic and elastoplastic properties of the material [10, 11, 12, 13, 14]. Speed of tensile machine grippers (in load increase and decrease) was 20% /min. The time for each relaxation was 10 minutes. Samples were manufactured in accordance with the standard ISO 527-2-5A with working part 2 on 4 by 20 mm.

4 Results discussion

The dependences of the nominal stress σ^0 on extension ratio λ for 12 loading cycles of a pure elastomer (NR) are shown in Fig. 1. The maximum step values of λ ranged from 1.5 to 7, increasing by 50% on each subsequent cycle. Unloading in each case was carried out until the stresses in the sample completely disappeared. These curves were used as the reference basis for comparison with the filled elastomers.

It was found that the pure rubber behaved almost like an elastic material up to an extension ratio $\lambda < 3.5$ (first 5 cycles). At large values of λ , it softened and began to exhibit viscoelastic properties (a hysteresis loop appeared, the curve of each new stretching was below the previous stretching curve). The residual deformations were insignificant, that is, we can assume that there were no plastic flows in pure rubber.

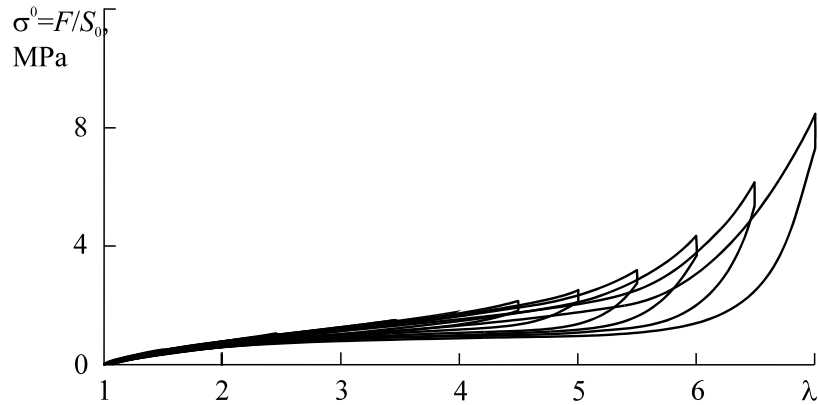


Figure 1: Cyclic stretching of pure natural rubber (NR): 12 cycles

The results of similar cyclic tests (12 cycles) for samples containing carbon black are shown in Figure 2. Adding 30 phr of CB significantly affected the mechanical properties of rubber:

First, the rigidity of the material has increased significantly. So, for example, in the samples filled with CB, maximum stresses on the second (maximum $\lambda = 2$), eighth ($\lambda = 5$) and twelfth ($\lambda = 7$) cycles increased approximately 3, 4 and 2 times, respectively, compared to the pure elastomer. At the same time, the differences between the unloading curves for filled and pure materials were significantly less.

Secondly, the dissipative losses increased significantly. The hysteresis of the load-unload curves was already observed on the second cycle, and, the larger the amplitude of the cycle tension, the stronger this effect was. The graphs show that there is also a significant softening of the material (Mullins effect [15, 16]) and it becomes viscoelastic.

Third, residual strains appeared in the filled samples.

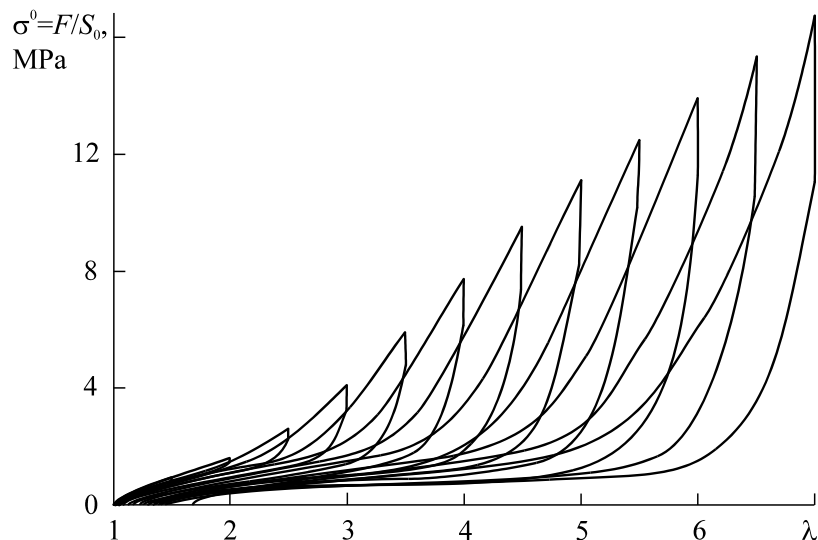


Figure 2: Curves of cyclic stretching of rubbers filled with carbon black (NR-CB30): 12 cycles

Therefore, the input of carbon black filler provokes the development of both reversible and irreversible rearrangements in the composite structure.

The following graphs show how the presence of clay filler affects the mechanical properties of rubber. Figure 3 demonstrates the results of cyclic loading (with stops at relaxation) samples NR-CB30 and NR-CB30-MMT5. Total twelve loading cycles are presented in Figure 3a, and only the first four (enlarged) in Figure 3b.

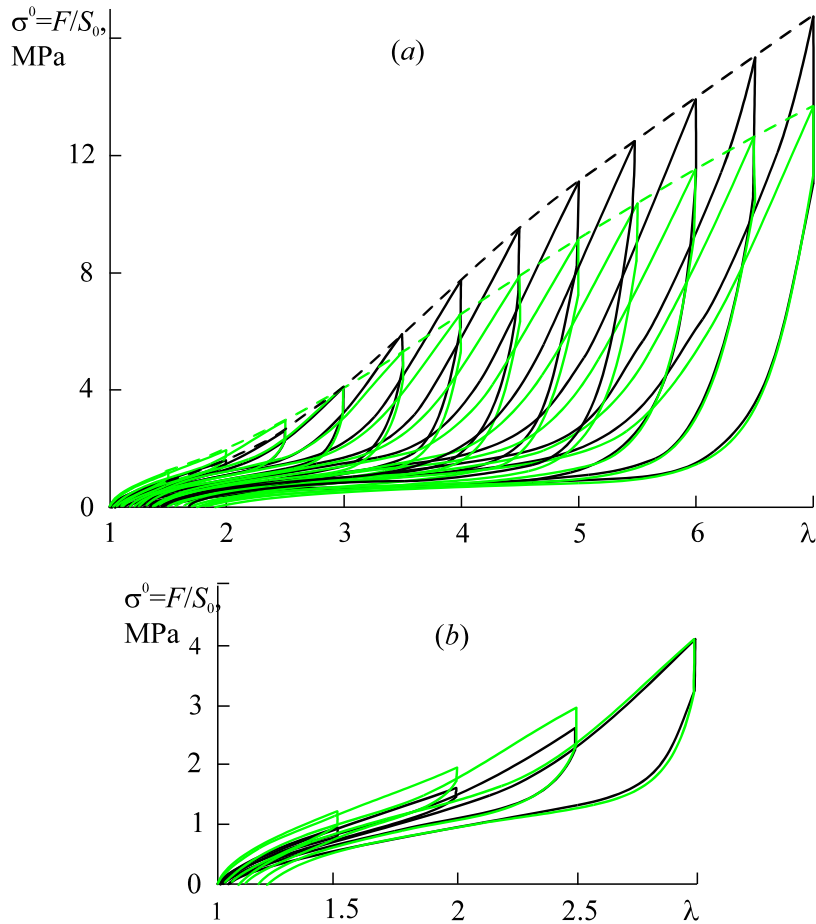


Figure 3: Curves of cyclic stretching of rubbers filled with CI and MMT. NR-CB30 — black lines, NR-CB30-MMT5 — green lines; (a) 12 cycles with full unloading on each of them; (b) 4 first cycles

At the initial stage of loading, the input of a clay nanofiller caused an increase in stresses compared to composites containing only CB. With further increase in the load, composites with clay nanoparticles became softer (compared to the systems "NR + CB"). For clarity, the dashed lines connecting the maximum stresses on the cycle for each material are plotted on the graphs.

In our opinion, this effect is due to the fact that at large extension ratios a re-orientation of the montmorillonite particles along the extension axis occurs in the composite structure. The plates in the tactoids can slip relative to each other under the influence of external deformation, thereby unloading the overstressed places. Consequently, less energy is required to deform the system and the level of macrostresses is reduced.

It is interesting to note that the unloading curves and residual deformations for these materials turned out to be close, that is, the introduction of montmorillonite affects these stages of cyclic loading poorly.

As a result, we can conclude that the addition of relatively small amounts of montmorillonite to the rubber significantly affects its mechanical properties, contributing to the development of both reversible and dissipative processes (viscoelastic and elastic-plastic) during deformation of the material. This is due to the peculiarities of the structure of the filler particles, which are bundles of parallel arranged ultrathin silicate plates.

Reorientation and distortion of the shape of these filler particles occurs in the process of composite material loading. It leads to a decrease in stress concentration at the level of microstructure and energy dissipation.

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