Experimental and theoretical basis for the creation of frost-resistant polymeric composite materials

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Experimental and theoretical basis for the creation of frost-resistant polymeric composite materials

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Abstract. The structural-mechanical behavior of a three-dimensional cross-linked elastomer, filled with solid particles under uniaxial tension were considered. This paper presents a theoretical and experimental basis for the development frost-resistant (glass transition temperature of ~170K), elastic (deformation of at least 70% at T=223K) polymer composite material. The equations of mechanical stresses dependence on deformation were used. Based on the results of numerical experiments, a frost-resistant elastic polymer composite material is simulated. The material was tested with a bursting machine and the experimental results were compared with the calculated data.

1. Introduction
Polymer composite materials with an elastomeric matrix filled with solid particles are widely used in parts and units of various structures in the automotive, aircraft and shipbuilding industries. The development of frost-resistant structural material for parts and components of various types of road and air transport operated in the Far North and the Arctic of Russia is an important engineering task. One of the problems is the creation of an elastic material that would be capable to operate at temperatures down to 170-223 K, would exhibit enhanced wear resistance, and could be prepared from cheap components.

The most promising way to solve this problem is the use of high-molecular-mass synthetic hydrocarbon rubbers in the form of copolymers that do not crystallize in a wide temperature range, as a polymer base of composites [1, 2]. The theory of structural-mechanical behavior of filled elastomer, developed in our previous studies [2], can be recommended for accelerating the development of such materials. In these studies we used the relationship between the mechanical failure energy and the composition of the three-dimensionally cross-linked plastized elastomer.

2. Theoretical foundations and characteristics used in calculations
The structural-mechanical behavior of a three-dimensional cross-linked plasticized elastomer filled with solid particles under uniaxial tension has been considered. The elastic potential of the spatial polymer network has the form:

\[ U = C_1(I_1 - 3) + C_2(I_2 - 3) . \]

The parameters \(2C_1\) and \(2C_2\) allowed Mooney and Rivlin [2] to write the equation:

\[ \sigma = (2C_1 + 2C_2\alpha^{-1})\alpha - \alpha^{-2}) . \]

Then as follows from [3]:
\[
\sigma = 2C_1(\alpha - \alpha^2) = \nu_c k T \alpha - \alpha^2 = \nu_c R T_{\infty} (\alpha - \alpha^2),
\]
where \( \sigma \) is the conditional stress (tensile force related to the initial cross section). Mooney-Rivlin equation in part of the influence of physical (intermolecular interactions) component cross-linking in a polymer binder was clarified (AS Ermilov and E Nurullaev [4]). In the final version the equation has the form:

\[
\sigma = \nu_c \rho_r^{1/3} RT_{\infty} \left\{ 1 + 29 \exp \left[ -0.225 \cdot 10^{-3} (T - T_g)^2 \right] \alpha^{-1} \alpha_b^{-1} \left( 1 + 1.25 \frac{\rho \phi_m}{1 - \rho \phi_m} \right) \right\}^{1/3}.
\]

The mechanical fracture energy of the filled elastomer is determined by the expression [4]:

\[
W = \left\{ \frac{\alpha_b^3 - 3\alpha_b + 2}{2\alpha_b} \right\} + 29 \exp \left[ -0.225 \cdot 10^{-3} (T - T_g)^2 \right] \alpha^{-1} \left( \frac{2\alpha_b^3 - 3\alpha_b + 1}{2\alpha_b^2} \right) \times \\
\times \left( \nu_c \rho_r^{1/3} RT_{\infty} \left( 1 + 1.25 \frac{\rho \phi_m}{1 - \rho \phi_m} \right)^2 \right).
\]

where: \( \alpha_b \) - tensile elongation; \( \nu_c \) - molar concentration of chemical transverse bonds in the polymer base of the binder; \( \rho_r \) - volume fraction of three-dimensional cross-linked polymer in the binder, \( R \) - universal gas constant; \( T_{\infty} \) - equilibrium temperature at which the concentration of "physical" (intermolecular) cross-links tends to zero; \( T \) - the test temperature of the sample; \( T_g \) - the temperature of structural glass transition of the polymer binder; \( \alpha_1 \) - the coefficient of speed equals to 1 at the standard relative speed of stretching; \( \rho \) - volume fraction of solid components; \( \phi_m \) – ultimate degree of volume filling depending on the particle shape and their fractional composition [4, 5].

Polymer composite material is created on the basis of high molecular mass three dimensional cross-linked elastomer polyisoprene divinyl. Synthetic rubber butadiene of isoprene with the catalyst compounds of lithium (SCDI-L) and plasticized with dioctylsebacinate has the following characteristics:

- molecular mass of 286000;
- structural glass transition temperature of 178 \( K \);
- density of 900 kg/m\(^3\) and a volume fraction of 0.4;
- a plasticizer with a glass transition temperature of 169 \( K \), a density of 910 kg/m\(^3\) and a volume fraction of 0.6;
- glass transition temperature of the elastomer \( T_g = 170 K \).

Value of fractional composition of silicon dioxide parameters are given in table 1.

| Fraction number | Weight-average particle size, \( \mu m \) | Limiting volume filling for fractions, \( \phi_{mi} \) | Optimum volume of fractions | Limiting volume filling of the mixture, \( \phi_m \) |
|-----------------|----------------------------------------|--------------------------|---------------------------|----------------------------|
| 1               | 1                                      | 0.535                    | 0.2                       |                            |
| 2               | 8                                      | 0.574                    | 0.30                      | 0.84                      |
| 3               | 240                                    | 0.633                    | 0.50                      |                            |

The calculated values were compared with experimental data using the program [6].
3. Results and discussion
The experimental and calculated diagrams of uniaxial extension at different temperatures for composite samples based on SLDI-L high-molecular-mass copolymer are shown in figure 1.

![Graph showing stress-strain relationship](image)

Figure 1. Stress $\sigma$ as a function of strain $\varepsilon$ for the composite based on SKDI-L at different temperatures of the experiment. Standard extension rate is $1.2 \times 10^{-3}$ s$^{-1}$. Solid lines: experimental data; dashed lines: data of numerical calculation.

Both the breaking stress and breaking strain increase with decreasing temperature. Such frost resistance of the elastomer composite can be associated with the extremely low structural glass transition point of the polymer binder. Such thermo-mechanical behavior of the composite based on SKDI-L copolymer is also influenced by the quinol ether as a cross-linking agent. In contrast to the quinol ether, sulfur-based rubber-vulcanizing systems form less strong chemical cross-links [4]. The corresponding envelopes, plotted in the extension diagrams of both kinds of composites according to T Smith, show that the breaking strain of the composite based on SKDI-L high molecular-mass copolymer considerably exceeds that of the composites based on a blend of SKD-KTR and PDF-3B low molecular-mass rubbers, whereas the breaking stresses for these composites differ only slightly as shown on figure 2.

The experimental and calculated dependences of the mechanical failure energy on the breaking stress are shown in figure 3. As can be seen, with a decrease in the test temperature and, naturally, with an increase in the intermolecular interaction, the mechanical failure energy determining the service life of a material regularly increases.

In all types of experimental verification of the developed theory of structural and mechanical behaviour of a filled three-dimensional cross-linked elastomer based on high-molecular divinyl isoprene rubber is shown to have a satisfactory convergence of the experimental data and the calculated characteristics (an error of the order of 5%, which is satisfactory for such problems).
4. Conclusion
The theoretical basis of the structural and mechanical behaviour of filled three-dimensional cross-linked elastomer has been improved. The corresponding numerical calculations are carried out. Based on the results of the numerical experiment, a frost-resistant, three-dimensional cross-linked, filled with three-fraction silicon dioxide plasticized elastomer is proposed. A satisfactory correlation between theoretical and experimental data is shown. The developed elastomer is proposed by the authors for use as gaskets in equipment, automotive and aircraft tires, operated in the Arctic and the Far North.
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