MACROMOLECULAR COMPOUNDS
AND POLYMERIC MATERIALS

Prediction of the Energy of Mechanical Failure
for Elastomers Filled with Solid Particles

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Abstract—Prediction (solution of direct problem) of the mechanical characteristics, including the energy of failure under extension, was considered for 3D-cross-linked elastomeric binders, filled with solid particles of polyfractional composition, in relation to the basic structural parameters of the composite material. It was shown that the use of lightly cross-linked highly silica-filled elastomeric binders with the optimal three-fraction composition represents a promising option for development of a frost-resistant waterproofing rolled material intended as a coating for road asphalt.

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Elastomers based on 3D-cross-linked low-molecular-weight rubbers (oligomers) with terminal functional groups, possibly plasticized, filled with solid polyfractional particles are widely used in various branches of industry. Of particular importance for these applications, e.g., in construction of buildings and structures, is long-term strength of polymer composite materials. For example, the development of frost-resistant waterproofing rolled materials for road asphalt coating requires polymeric compositions with enhanced deformation resistance over a broad range of operation temperatures.

Here, we examined how selected structural (formulation) factors affect the energy of mechanical failure of a specified filled elastomer intended as a coating for asphalt of roads located in sharply continental climate zones.

The energy (work) of failure was estimated in the form of an “envelope” [1] of the dependence of the nominal breaking tensile stress $\sigma_b$ (breaking stress based on the initial cross-sectional area) on the breaking elongation $\alpha_b$ related to the degree of relative breaking elongation ($\alpha_b = 1 + \varepsilon_b/100\%$). The logarithmically plotted failure envelope curve ($\log \sigma_b$-$\log \varepsilon_b$), connecting the breaking points of the specimens, corresponds to the work of mechanical failure in the form of the area of the extension diagram in Cartesian coordinates:

$A_b = \int_1^{\sigma_b} \sigma(\alpha) d\alpha,$  \hspace{1cm} (1)

where the structural-mechanical relationship between the conditional stress $\sigma$ and the elongation $\alpha$ in the absence of exfoliation of the filler particles from the elastomeric binder in the asphalt coating was substantiated by us previously [2]:

$\sigma(\alpha) = \nu_{ch} \phi_r^{1/3} R T_\infty \{1 + 29 \exp(-0.225 \times 10^{-3} (T - T_g)^2)) \times \alpha^{-1} \alpha_a^{-1} \left(1 + 1.25 \frac{\phi/\phi_m}{1 - \phi/\phi_m}\right)^2 (\alpha - \alpha^2)^{-1},$  \hspace{1cm} (2)

Here, $\nu_{ch} = \rho/M_c$ is the molar concentration of chemical cross-links in the polymeric base of the binder ($\rho$ is the density of the polymer, and $M_c$, statistical average molecular weight of the segments between cross-links); $\phi_r$, volume fraction of the polymer in the binder containing a plasticizer; $R$, universal gas constant; $T_\infty$, equilibrium temperature [at which the concentration of “physical” (intermolecular) cross-links $\nu_{ph}$ is negligible]; $T$, test temperature; $T_g$, structural glass transition point of the polymeric binder; $\alpha_a$, velocity shift coefficient ($\alpha_a = 1$ at $\alpha = 1.4 \times 10^{-3}$ s$^{-1}$, which is the industry-specific standard value); $\phi$, volume fraction of dispersed filler; and $\phi_m$,..
maximal volume fraction of the filler in elastomer, which depends on the shape and fractional composition of the filler particles, as well as on physicochemical interaction at the filler–binder interface. The \( \phi_m \) quantity can be calculated by the combinatorial multiplicative method [3] or determined viscometrically [4].

The \( \alpha_\phi \) parameter in Eq. (1), similarly to \( \epsilon_\phi \), is determined from the formula [1]

\[
\alpha_\phi = \alpha_\phi^0 (1 - 3\phi/\phi_m) + 3\phi/\phi_m, \quad \epsilon_\phi = \epsilon_\phi^0 (1 - 3\phi/\phi_m), \quad (3)
\]

where the superscripts “f” and “0” refer to the filled and unfilled elastomers, respectively.

The breaking elongation of the elastomeric binder \( \epsilon_\phi^0 \), determined by the effective concentration of cross-links \( \nu_{\text{eff}} = \nu_{\text{ch}} + \nu_{\text{pl}} \), was derived experimentally [1].

As frost-resistant polymeric base for the asphalt waterproofing rolled material served a 3D-cross-linked noncrystallizing copolymer of two low-molecular-weight rubbers with terminal functional groups: epoxy (–CH(O) CH\(_2\), polye diene urethane epoxy PDI-3B grade rubber) and carboxy (–COOH, polybutadiene SKD-KTR grade rubber) in a 1:2 molar ratio. The cross-linking agent was EET-1 trifunctional epoxy resin taken in different concentrations with the mixture of PDI-3B and SKD-KTR rubbers. This yielded elastomeric compositions with different concentrations of chemical cross-links \( \nu_{\text{ch}} \) in the polymeric base. By contrast to bitumen binder of asphalt, the resulting binders retained their elastomeric (rubbery) properties down to 223 K (–50°C). The introduction of plasticizer \( (\phi_{\text{pl}} = 1 - \phi, = 0.3) \), dioctyl sebacate, caused the structural glass transition point of the binder to decrease to 213 K.

The \( \nu_{\text{ch}} = \rho/M \bar{M} \) quantity was calculated using the corresponding molecular graph:

\[
[M]_\alpha = ([f_{32}]_2 - R_3 - f_{32} - R_2 - f_{21} - (-R_1 - f_{12} - R_2 - c)_n - f_{23} - R_3 - (f_{32} - c)_2]_\alpha,
\]

where the combination of subscripts under \( f \) and \( R \) refer to the instantaneous molecular fragments as the products of reactions of \( i \) th and \( j \) th antipodal terminal functional groups of PDI-3B \( (R_1) \) and SKD-KTR \( (R_2) \) rubbers and cross-linking agent EET-1 \( (R_3) \). At equimolar ratio of the polymeric base components \( R_1:R_2:R_3 = 1:2:1 \), index \( n \) is equal to unity.

The effective concentration of cross-links \( \nu_{\text{eff}} \), including the intermolecular (“physical”) component depending on \( (T - T_\phi) \) in accordance with Eq. (2), was chosen at three levels: \( 1 \times 10^{-5}, 3 \times 10^{-5}, \) and \( 5 \times 10^{-5} \) mol \( \text{cm}^{-3} \). These values correspond to the experimental dependence \( \epsilon_\phi^0 = f(\nu_{\text{eff}}) \) normalized to 293 K [2], specifically, to 1100, 900, and 600% breaking elongations of unfilled elastomeric binder, respectively.

The volume fraction \( \phi \) of the filler, silica (river quartz sand), was 0.65, so that the content of a more expensive component, polymeric binder, could be decreased. We used a three-fraction mixture of silicas with the optimal size grading 600 \( \mu \text{m}: 30 \mu \text{m}: 1 \mu \text{m} = 0.68 : 0.24 : 0.08 \).

The calculations of \( \phi_m \) and optimization of the fractional composition of the filler to a maximal value were carried out with the use of the appropriate software [5] containing the data on the weighted-average particle sizes of individual silica fractions obtained by mechanical grinding. The maximal volume fraction of the filler \( \phi_{\text{mt}} \) calculated with physicochemical interaction at the filler–binder interface taken into account [4], was 0.921.

For predicting the energy of mechanical failure of the specimens we used the software [6] which was designed by us earlier for the development of a frost-resistant waterproofing road asphalt coating.

Figure 1 shows the calculated stress-elongation diagrams for the filled elastomer having the molar effective concentration of cross links \( \nu_{\text{eff}} = 1 \times 10^{-5} \) mol \( \text{cm}^{-3} \) (at the reference temperature of 293 K), obtained by modeling at different temperatures. Similar \( \sigma = f(\alpha) \) dependences were calculated for \( \nu_{\text{eff}} = 3 \times 10^{-5}, \nu_{\text{eff}} = 5 \times 10^{-5} \) mol \( \text{cm}^{-3} \). The table lists the corresponding mechanical characteristics of the elastomeric composites, predicted under different temperatures: initial viscoelastic modulus \( E \), breaking stress \( \sigma_b \), and breaking elongation \( \epsilon_b \).

It is seen from the tabulated data that lightly cross-linked polymeric bases represent the preferred option for the development of a frost-resistant elastomeric coating for road asphalt.

Figure 2 shows the failure envelopes for the designed breaking points of the filled elastomers, plotted in the direct-scale logarithmic coordinates of the \( \sigma_b, \epsilon_b \) mechanical characteristics. It is seen that the energy of mechanical failure for the specimens tends to increase with increasing concentration of chemical cross-links in the polymeric base. It is worthy of note that, as the modeling temperature decreases, the failure envelopes approach one another. The reason is that, at negative Celsius temperatures, the number of intermolecular (physical) cross-links exceeds