Dependence of mechanical characteristics from composition and structure and optimization of mechanical fracture energy of polymer composite material based on high-molecular rubbers

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ABSTRACT. By means of numerical experiment the authors investigate dependence of conventional rupturing stress and mechanical fracture energy at uniaxial tension from fractional composition of dispersed filler, plasticizer volume fraction in polymer binder, effective density of transverse bonds, applied to development of covering for different purposes and with advanced service life in temperature range from 223 to 323 K.

They compare mechanical characteristics of polymer composite materials (PCMs) based on high- and low-molecular rubbers. It was shown that rupturing stress of high-molecular rubber-based PCM is of a higher magnitude than the stress of low-molecular rubber-based one at almost invariable rupturing deformation.

Numerical simulation by variation of composition parameters and molecular structure enables evaluation of its maximum fracture energy which is 1000 times higher than mechanical fracture energy of similar composites based on low-molecular rubbers.

KEYWORDS. High-molecular rubbers; Deformation; Composites; Mechanical stress; Envelopes of fracture points; Optimization; Plasticizer; Polymer composite; Linking; Glass transition temperature.

INTRODUCTION

Fractional composition of dispersed filler is very essential both for formation of rheological properties of suspensions based on viscous-liquid polymer binders and mechanical characteristics of 3D-linked filled polymer composite materials (PCMs). At that basic formulation parameter is effective extent of volume filling – ϕ / ϕ_m, where ϕ is volume fraction of filler solids, ϕ_m - maximum volume filling depending on particle shape, fractional composition and physicochemical interaction on filler – binder interface.

Structural and mechanical dependence of conventional stress (σ) from relative elongation degree (α) in case of no lamination between filler particles and polymer binder, for example in road asphalt covering, was proved in previous work [1].

Nowadays it is important to develop polymer composite material [2] as a covering for roofs of residential and industrial buildings, sports grounds, and road asphalt with advanced service life in comparison with commonly used PCM.

To accelerate development of mentioned polymer composites, it is necessary first of all to investigate relation between molecular structure of polymer binder, effective extent of volume filling, mechanical characteristics and mechanical fracture energy of PCM [3]. Previously we have shown that effective mole concentration of transverse chemical and intermolecular bonds is key structural parameter of 3D-linked elastomers filled with solids and based on low-molecular rubbers with terminal functional groups [4].

Unfortunately mechanical characteristics of 3D-linked rubbers are usually evaluated without construction of envelopes of sample rupture points according to T. L. Smith at uniaxial tension and different temperatures and deformation rates [3, 5]. The latter enable to predict service life of advanced PCM in different coverings.

This work is intended to investigate numerically the dependence of conventional rupturing stress and mechanical fracture energy at uniaxial tension from fractional composition of dispersed filler, plasticizer volume fraction in polymer binder, effective density of transverse bonds, applied to development of covering for different purposes and with advanced service life in temperature range from 223 to 323 K.

OBJECT OF NUMERICAL EXPERIMENT

Object of numerical experiment is 3D-linked polymer composite material based on mixture of high-molecular rubbers: isoprene of grade IR and butadiene of grade BR. [6, 7].

Linking agent – sulfur; vulcanization accelerator – tetralkyltiuramdisulfide ("tiuram-D"); catalyst of cross-linking reaction – zinc oxide [6].

Plasticizing oil is used as a plasticizer [7]. Dispersed filler – silica (silicon dioxide, silica sand) with different fractional compositions.

THEORETICAL PART

Computer prediction (calculation) for diagram of uniaxial tension of filled elastomer sample is based on description of its structural and mechanical behavior [1]. At that dependence of conventional (related to initial cross-section of the sample) stress (σ) from relative elongation (α), which is related to deformation (ε) by the expression: α = 1+ε/100%, comprises following basic structural parameters and deformation conditions:

$\nu_{ch} = \rho / \overline{M_c}$, where ρ is polymer density, $\overline{M_c}$ – average internodal molecular weight of the polymer binder;

$\varphi_r = 1 - \varphi_{sw}$ – polymer volume fraction in the composite binder, ϕ_{sw} – plasticizer volume fraction in the binder;

R – universal gas constant;

T_∞ – equilibrium temperature, at which concentration of "physical" (intermolecular) bonds (ν_{pb}) is negligible;

T_g – glass transition temperature of the polymer binder;

T – sample test temperature (of numerical experiment);

$a_{\dot{\alpha}}^{-1}$ – velocity shift coefficient, $a_{\dot{\alpha}}^{-1} = 1$ at standard relative extension rate $\left(\dot{\alpha}, c^{-1} \right)$ accepted for science and industry;

φ – filler volume fraction;

φ_m – maximum filler volume fraction, depending on fractional composition, particle shape and physicochemical interaction on the filler – binder interface. Basic equation is as follows:

$$\sigma = \nu_{ch} \varphi_r^{1/3} R T_\infty \left\{ 1 + 29 \exp\left[-0.225 \cdot 10^{-3} \left(T - T_g \right)^2 \right] \alpha^{-1} a_{\dot{\alpha}}^{-1} \right\} \cdot$$

$$\left\{ 1 + 1.25 \frac{\varphi/\varphi_m}{1 - \varphi/\varphi_m} \sum_{i=1}^{n} \left[1 - \frac{1}{\sqrt{2\pi}} \int_1^\infty \exp\left(-0.5 t_i^2 \right) dt_i \right] \varphi_i \right\}^2 \left(\alpha - \alpha^{-2} \right)$$

where accumulation kinetics of internal composite damage as lamination between the polymer binder and filler particles is described in Gaussian function; n – quantity of volume fractions φ_i of delaminated dispersed filler fractions (types); $t_i = (\alpha - \alpha_{0.5i}) / \bar{\sigma}_{si}$ – function parameter, $\alpha_{0.5i}$ – sample elongation corresponding to the half volume of delaminated particles with i–type filler fraction (type), $\bar{\sigma}_{si}$ – mean-square dispersion for i–type filler fraction (type). Value $\alpha_{0.5i}$ determines delimitation initiation, $\bar{\sigma}_{si}$ characterizes composite integrity violation rate.

As long as there is no the interfacial Delamination in the elastomeric composite, limiting (rupturing) mechanical characteristics σ_b, a_b can be evaluated by considering of deformation rate and size of average polymer binder interlayer between filler solids:

$$\dot{\alpha}_f = \dot{\alpha}_0 \left(1 - \sqrt[3]{\varphi/\varphi_m}\right) + \sqrt[3]{\varphi/\varphi_m}; \qquad \alpha_b^f = \alpha_b^0 \left(\sqrt[3]{\varphi/\varphi_m} + \sqrt[3]{\varphi/\varphi_m}\right)$$

where indexes «f» and «o» stand for filled and free state elastomeric, respectively. In terms of rupturing deformation the following relation results:

$$\varepsilon_b^f = \varepsilon_b^0 \left(1 - \sqrt[3]{\varphi/\varphi_m}\right)$$

Value ε_b^0 is derived out of the curve $\varepsilon_b^0 = f\left(v_{eff}\right)$ which was obtained earlier by summarizing of multiple experimental data [1]. Effective concentration of transverse bonds is equal to the total concentrations of chemical (determinant for 3D-linking of initial linear polymers) and physical (intermolecular, depending on polymer structure and experiment temperature) bonds:

$$v_{eff} = v_{ch}\phi_r^{1/3}(1 + v_{ph}) = v_{ch}\phi_r^{1/3}\left\{1 + 29\exp\left[-0{,}225{\cdot}10^{-3}(T - T_g)^2\right]\right\}$$

For example, if $v_{eff} = 1\,mol/m^3$ and $T = 293K$ rupturing deformation of 3D-linked elastomeric binder ε_b^0 is almost 1000%. Stated curve is part of the computer program as a calibrating one [8].

If sample integrity has been damaged up to the rupture, limiting mechanical characteristics are maximum point values for hump-shaped tension diagrams (σ_{max}, ε_{max}) or values of constrained maximum point assuring serviceability of partly disrupted composite, despite of possible sample tension.

To evaluate dependence of material service time from internal damage level of filled polymer composite material by tension, we use envelopes of sample fracture points if no laminations (σ_b, ε_b) or maximum points mentioned above (σ_{max}, ε_{max}). These envelopes were introduced by Smith as following dependences "$\log\sigma_{b,max} - \log\varepsilon_{b,max}$" [9, 10].

Problem of fractional composition optimization for dispersed components of polymer material (for given average particle sizes) considering fulfillment of optimization conditions for other performance characteristics could be defined in the following nonlinear programming statement:

$$\varphi_m(\vec{\varphi}, \vec{q}, \vec{d}) \Rightarrow \max; \quad \eta_r \Rightarrow \min; \quad E_r \Rightarrow \min; \qquad \varphi_j^{opt} = \varphi_{j1} + \varphi_{j2} + \varphi_{j3} + ... + \varphi_{jm_j} = \sum_{v=1}^{m_j} \varphi_{jv};$$

$$0 \le \varphi_{jv}^{min} \le \varphi_{jv} \le \varphi_{jv}^{max} \le 1, \ v = 1,\ 2,\ 3,\ ...,\ m_j \ \text{if} \ \forall \ j \in I_n; \qquad \varphi_j^{opt} = \frac{x_j^{opt}/\gamma_j}{\sum\limits_{j \in I_n} x_j^{opt}/\gamma_j},$$

where $\vec{\varphi}, \vec{q}, \vec{d}$ are vectors of volume fractions, porosities and particle sizes of dispersed components in the polymer material, respectively, φ_j^{opt} is optimal volume fraction of the filler in the composition, φ_{jv} – volume fraction of v-th fraction with j-type filler in the composition, m_j – fraction number of j-type dispersed component, φ_{jv}^{min}, φ_{jv}^{max} are upper and lower limits for solids volume fractions in the composition, respectively, x_j^{opt} is optimum mass concentration of solid

dispersed ingredients in the polymer composition for corresponding characteristics set, for example mechanical, γ_j are densities of dispersed components, I_n is variety of indexes for filler types being part of polymer material formulation.

Because of the difficulty, given problem which includes limitation of equation types is converted into the nonlinear programming problem with limitation of in equation types. At that quantity of optimizable independent variables is $n = (m_j) - m$, where m is quantity of polymer material solids types. Normalizing ratio:

$$\sum_{j \in I_n} \sum_{v=1}^{m_j} \varphi_{jv} = \sum_{j \in I_n} \varphi_j^{opt} = 1$$

is automatically fulfilled in case of problem solution.

Then we determine the vector of optimum volume fractions for filler fraction in the composition:

$$\vec{\varphi}^{opt} = (\vec{\varphi}_{jv}^{opt}; \; \forall_j \in I_n); \quad v = 1, \; 2, \; 3, \; ..., \; m_j ,$$

where φ_{jv}^{opt} is optimum volume fraction of v-th fraction for j-type filler.

Transformation to optimum mass concentrations of the corresponding solids

$$\vec{x}_j^{opt} = (\vec{x}_{jv}^{opt}; \; \forall_j \in I_n; \; v = 1, \; 2, 3, \; ..., \; m_j)$$

is carried out by formula:

$$x_{jv}^{opt} = (\phi_{jv}^{opt} \gamma_j) / (\phi_j^{opt} / \gamma_j) \cdot P, \quad \text{where}$$

$$P = \sum_{j \in I_n} \sum_{v=1}^{m_j} x_{jv}^{opt} = \sum_{j \in I_n} x_j^{opt}$$

is the sum of mass concentrations (ratios) of polymer material solids.

Mechanical fracture energy (W) of PCM depending on rupturing elongation degree (α_b) is calculated by formula [11]:

$$W = \nu_{ch} \varphi_r^{1/3} RT_\infty \left(1+1.25\frac{\varphi/\varphi_m}{1-\varphi/\varphi_m}\right)^2 \left\{\left[\left(\frac{\alpha_b^3-3\alpha_b+2}{2\alpha_b}\right)+29\exp\left[-0/225\cdot10^3\left(T-T_g\right)^2\right]a_{\ddot{\alpha}}^{-1}\left(\frac{2\alpha_b^3-3\alpha_b^2+1}{2\alpha_b^2}\right)\right]\right\} \tag{1}$$

Mathematical problem statement for maximum fracture energy search when limitations of other characteristics are fulfilled can be described as following nonlinear programming problem:

$$\left.\begin{cases} W\left(\overline{v_{ch}}, \; \overline{\varphi_r}, \; \overline{\varphi/\varphi_m}\right) \text{ - max} \\ 0.1\cdot10^{-5}\leq(v_{ch})_i\leq2\cdot10^{-5} \\ 0.3\leq(\varphi_r=1-\varphi_{sw})_i\leq0.7 \\ 0.5\leq(\varphi/\varphi_m)_i<1 \end{cases}\right\} \left(\forall_i \in I_n\right) \tag{2}$$

where:

$\overline{v_{ch}}$, $\overline{\varphi_r}$, $\overline{\varphi/\varphi_m}$ – vectors of cross-linking mole concentration, polymer volume fraction in the binder and effective extent of volume filling, respectively;

φ_{sw}– plasticizer volume fraction, coherent with polymer volume fraction (φ_m) as ratio $(\phi_r + \phi_{sw}) = 1$;

I_n – variety of indexes for composition; n –quantity of composition calculation types.

NUMERICAL EXPERIMENTATION

Tab. 1 presents optimized parameter values of silica fraction mixtures in the PCM which are calculated using computer program being developed by the authors [8]. Numerical experiments are carried out for: $v_{ch} = 3 \; mol/m^3$, which is chosen according to predesigned as most effective one. Plasticizer volume fractions in the polymer binder are chosen in form of three values 0.05; 0.1; 0.3 to provide development of the PCM with low viscosity. The last one is required for good component mixing. Tab. 2 presents data required for numerical experimentation.

Fraction number	Particle diameter, M	Void volume ratio	Optimum values of fraction volume ratio	Maximum volume filling
		Two fractions		
1	15	0.386	0.2	0.84
2	600	0.244	0.8	
		Three fractions		
1	1	0.465	0.05	
2	15	0.386	0.149	0.94
3	600	0.244	0.801	
		Four fractions		
1	1	0.465	0.028	
2	15	0.386	0.082	0.96
3	240	0.367	0.226	
4	600	0.244	0.664	

Table 1: Optimum parameter values of silica fraction mixtures.

Fraction quantity	2; 3; 4
Experiment temperature, K	223; 273; 323
Glass transition temperature of the polymer 1 (isoprene of IR grade) K	200
Glass transition temperature of the polymer 2 (butadiene of BR grade), K	178
Molecular weight of the polymer 1 (isoprene of IR grade)	372802
Molecular weight of the polymer 2 (butadiene of BR grade)	198775
Density of the polymer 1 (isoprene of IR grade) kg/m^3	900
Density of the polymer 2 butadiene of BR grade) kg/m^3	890
Volume fraction of the polymer 1 (isoprene of IR grade) in the binder	0.7; 0.65; 0.5
Volume fraction of the polymer 2 (butadiene of BR grade) in the binder	0.25; 0.25; 0.2
Volume fraction of the filler	0.75
Chemical bond density, mol/m^3	3
Design glass transition temperature of the rubber, K	192.3
Molecular weight of the plasticizer (plasticizing oil of MPA grade)	1010
Glass transition temperature of the plasticizer, K	169
Density of the plasticizer, kg/cm^3	890
Volume fraction of the plasticizer	0.05; 0.1; 0.3

Table 2: Data required for numerical experimentation.

Tab. 3 presents numerical experimentation results about dependence of rupturing stress from rupturing deformation of the PCM depending on plasticizer volume fractions in the binder from 0.05 to 0.3 *vol. fraction*, on filler fraction

composition. Analysis of numerical experimentation results has shown, that increase of plasticizer volume fraction from 0.05 to 0.3 (experiment temperature is 223 K; four – fraction silica) causes decrease of rupturing stress (from 12 to 9 *MPa*) at slight deformation increase (from 26 to 27%,). Experiment temperature increase does not change this tendency (Tab. 3). Increase of silica fraction quantity in the PCM from two to four causes decrease of conventional rupturing stress from 28 to 11 *MPa* at rupturing deformation increase from 12 to 26% (numerical experiment temperature is 223 K, 0.1 vol. fraction plasticizer). If $T = 273 K$, 0.1 vol. fraction plasticizer, conventional rupturing stress decreases from 12 to 4 *MPa* at deformation increase from 17 to 36%; if $T = 323 K$ – from 3 *MPa* (22%) to 1 *MPa* (45%).

Basic requirements to different coverings, especially to road asphalt, are the followings: rupturing stress – ap. 8 *MPa* and deformation – at least 12 – 15% at the temperature 223K.

	Plasticizer volume fraction $\varphi_{sw} = 0.05$ *vol. fraction*								
	Dispersed filler								
	Two-fraction silica			Three-fraction silica			Four-fraction silica		
	Experiment temperature. *K*			Experiment temperature. *K*			Experiment temperature. *K*		
	223	273	323	223	273	323	223	273	323
$\sigma_b.$ *MPa*	29	12	3	5.5	2.1	0.6	12	4	1
$\varepsilon_b.$ %	12	16	22	42	58	75	26	36	45
	Plasticizer volume fraction $\varphi_{sw} = 0.1$ *vol. fraction*								
$\sigma_b.$ *MPa*	28	12	3	7	2.6	0.75	11	4	1
$\varepsilon_b.$ %	12	17	22	37	52	64	26	36	45
	Plasticizer volume fraction $\varphi_{sw} = 0.3$ *vol. fraction*								
$\sigma_b.$ *MPa*	25	9	2	6	2	0.6	9	3.2	1
$\varepsilon_b.$ %	13	18	22	38	54	65	27	39	47

Table 3: Numerical experimentation results about dependence of rupturing stress from rupturing deformation of the PCM.

According to the Tab. 3, PCM based on 3D-linked high-molecular rubbers, filled with four silica fraction mixture at plasticizer volume fraction 0,05 in the binder, fully complies with given requirements.

Fig. 1 presents envelopes of rupture points for the PCM according to T. L. Smith for different filler fraction values at 0.05 plasticizer volume fraction in the binder and cross-binding concentration $v_{ch} = 3$ *mol/m³* at different temperatures of numerical experiment. It is obvious, that PCM filled with optimum mixture of four silica fractions meets the requirements to different coverings, especially to road asphalt.
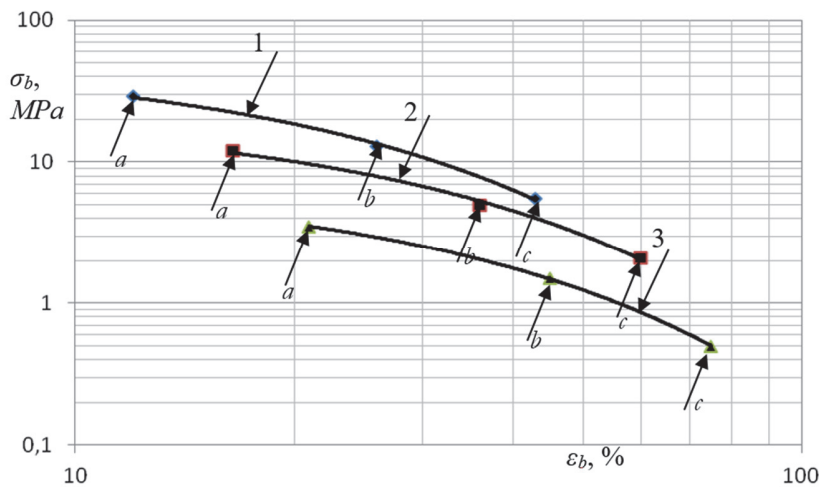

Figure 1: Envelopes of rupture points for polymer composite material according to T. L. Smith for different filler fraction values at 0.05 plasticizer volume fraction in the binder and $v_{ch} = 3$ *mol/m³* at different temperatures of numerical experiment. Experiment temperature: 1 – 223 *K*; 2. – 273 *K*; 3. – 323 *K*; *a* - Two-fraction silica; *b* - Four-fraction silica; *c* - Three-fraction silica.

Previously the authors have proposed polymer composite material for road covering based on low-molecular rubbers of butadiene + dieneepoxyetherurethane [12]. For comparison of mechanical behavior of low-molecular and high-molecular rubber-based PCMs, Fig. 2 presents envelopes of rupture points for polymer composite materials according to T. L. Smith.
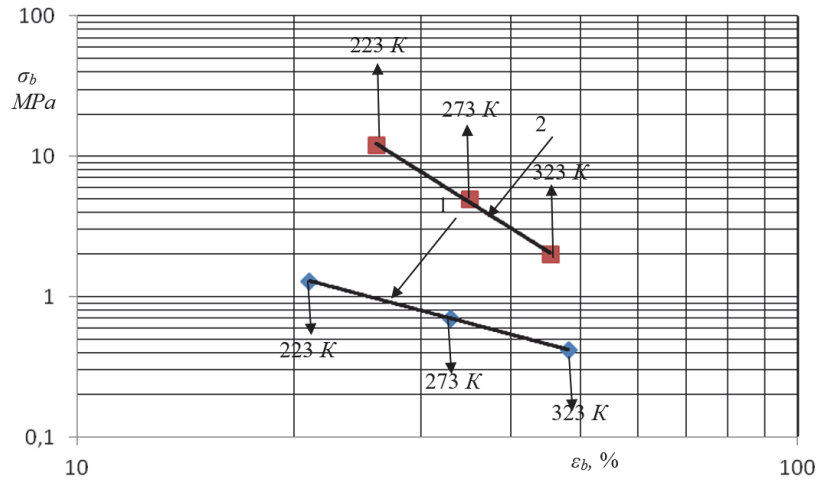

Figure 2: Envelopes of rupture points for polymer composite materials according to T. L. Smith: 1 – based on low-molecular rubbers BR-KTR + PDI- 3B; 2 – based on high-molecular rubbers IR + BR-

It is obvious that rupturing stress of PCM based on high-molecular rubber mixture is of a higher magnitude than of the low-molecular rubber-based one (12 against 1.2 *MPa)*, at almost the same rupturing deformation.

Plasticizer volume fraction $\varphi_{sw} = 0,05$ *vol. fraction*								
Dispersed filler								
Two-fraction silica			Three-fraction silica			Four-fraction silica		
Experiment temperature, *K*			Experiment temperature, *K*			Experiment temperature, *K*		
223	273	323	223	273	323	223	273	323
1800	1100	400	1500	850	300	1700	920	350
12	16	25	35	50	70	30	46	55
Plasticizer volume fraction $\varphi_{sw} = 0,1$ *vol. fraction*								
1750	1050	350	1400	800	300	1550	900	320
12	17	22	40	55	70	26	36	50
Plasticizer volume fraction $\varphi_{sw} = 0,3$ *vol. fraction*								
1650	900	300	1350	700	250	1500	750	300
13	18	22	38	54	65	27	37	45

Note: In first column of data rows: *W, kJ* and $\varepsilon_b, \%$

Table 4: Numerical experimentation results by determination of maximum mechanical fracture energies for PCM.

DETERMINATION OF MAXIMUM FRACTURE ENERGY OF FILLED PLASTICIZED POLYMER COMPOSITE MATERIAL

Mechanical fracture energy is optimized for $v_{cb} = 3$ *mol/m³*. Plasticizer volume fractions in the binder are chosen in form of three values: 0.05; 0.1; 0.3.

Tab. 4 presents numerical experimentation results by determination of maximum mechanical fracture energy for PCM.

Analysis of simulated results has shown, describes dependence between mechanical fracture energies and PCM fraction composition. It is obvious, that increase of fraction quantity causes decrease of fracture energy from 1800 to 1650 kJ at

the temperature 223 K, and rupturing deformation increases from 12% to 35%; at 273 K – from 1100 to 900 kJ; rupturing deformation – from 16% to 46%; at 323 K – from 400 to 350 kJ, rupturing deformation – from 25% to 55%.

Fig. 3 presents for the first time by the authors constructed envelopes mechanical destruction energy values for the four fractions of silicon dioxide at a volume fraction of the plasticizer - φ_{sw} = 0.05 and temperatures of numerical experiment 223 K, 273 K, 323 K.

Envelopes of rupture points of polymer composite material according to T. L. Smith qualitatively characterize material service time. In contrast to that, envelopes of mechanical fracture energies quantitatively evaluate service Life of PCM.

Envelopes of mechanical fracture energies for PCM based on low-molecular and high-molecular rubber mixtures are constructed for comparison (Fig. 4). It was shown, that mechanical fracture energy of PCM based on high-molecular rubber mixture is 1000 times higher than of the low-molecular rubber-based one.
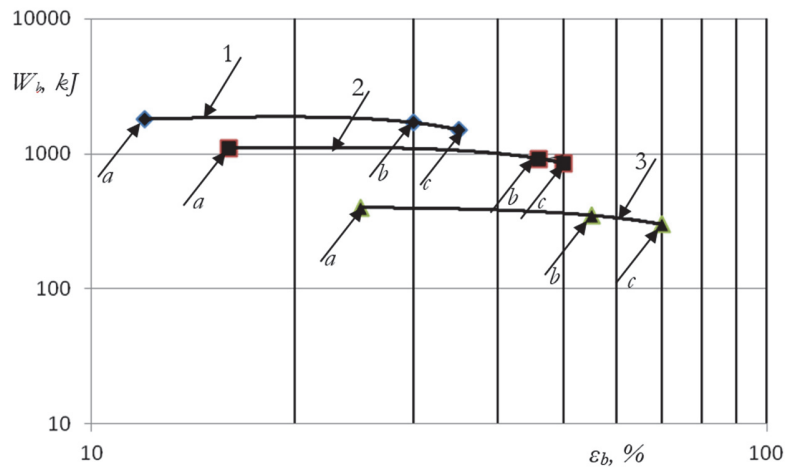

Figure 3: Envelopes of mechanical fracture energies. φ_{sw} = 0.05; vol. fraction; Experiment temperature: 1 – 223 K; 2 – 273 K; 3 – 273 K. *a* - Two-fraction silica; *b* - Four-fraction silica; *c* - Three-fraction silica
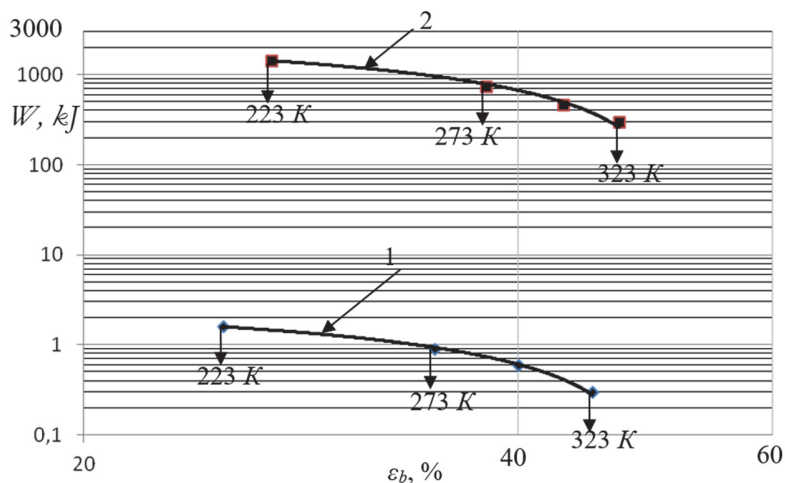

Figure 4: Envelopes of mechanical fracture energies for PCM: 1 – based on low-molecular rubbers BR-KTR + PDI- 3B; 2 – based on high-molecular rubbers IR + BR.

CONCLUSIONS

1. Optimized parameter values of silica fraction mixtures in polymer composite materials are calculated using computer program being developed by the authors.

2. Increase of silica fraction quantity in the composite from two to four causes decrease of conventional rupturing stress at rupturing deformation increase at every temperature of numerical experiment.

3. For the first time the authors constructed envelopes of sample rupture points according to T. Smith at uniaxial tension and different temperatures, plasticizer volume fractions in the polymer binder and different filler fraction mixture values, which enable basically predict service live of advanced polymer composite materials in different coverings.

4. To compare mechanical behavior of composites based on low-molecular and high-molecular rubbers, envelopes of rupture points are constructed according to T. L. Smith. It is shown that rupturing stress of covering material based on high-molecular rubbers is far above than of the low-molecular ones.

5. It is shown, that composite filled with optimum mixture of four silica fractions at plasticizer volume fraction 0.05 in the binder fully complies with given requirements to different coverings, especially to road asphalt.

6. Maximum mechanical fracture energy for filled composite material is determined. It is shown, that mechanical fracture energy maximizes when the polymer binder is filled with four-fraction silica.

7. For the first time the authors constructed envelopes of mechanical fracture energies depending on plasticizer volume fraction, fraction composition of polymer composite material and experiment temperature. It is stated, that mechanical characteristics, first of all mechanical fracture energy, maximizes at plasticizer volume fraction $0.05 - 0.3$ volume fractions in the binder from operating temperature.

8. It is stated, that mechanical fracture energy of polymer composite material based on high-molecular rubbers is 1000 times higher than of the low-molecular rubber-based one

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