Dependence of the mechanical fracture energy of the polymeric composite material from the mixture of filler fractions

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ABSTRACT. This paper for the first time presents an equation for calculating the mechanical fracture energy of the polymeric composite material (PCM) with regard to the basic formulation parameters. By means of the developed computer program the authors calculated the mechanical fracture energy of the polymer binder of the 3D cross-linked plasticized elastomer filled with multifractional silica.

The solution of the integral equation was implemented using the corresponding dependence of stress on relative elongation at uniaxial tension. Engineering application of the theory was considered with respect to asphalt road covering.

The authors proposed a generalized dependence of ruptural deformation of the polymer binder from the effective concentration of chemical and physical (intermolecular) bonds for calculating the mechanical fracture energy of available and advanced PCMs as filled elastomers.

KEYWORDS. Energy failure; Elastomeric; Particulate filler; Binder; Polymer composite material.

INTRODUCTION

Nowadays, the current issue of technical chemistry is to ensure the required deformation and strength characteristics of advanced polymeric composite materials, in particular, 3D cross-linked filled plasticized elastomers.

So far, to estimate the effect of the basic formulation parameters on the mechanical properties of such materials at uniaxial tension, Smith failure envelopes have been widely used [1-4]. However, this approach does not fully reflect the physical nature of the failure (or fracture) process. Therefore, it is interesting to derive an equation for calculating the mechanical fracture energy as a composite performance indicator of 3D cross-linked polymeric composite materials.

The objective of this paper is a mathematical derivation of the equation for calculating the mechanical fracture energy of polymeric composite materials with regard to the basic formulation parameters by integrating the equation that describes the curve of uniaxial tension.

In addition, by means of the computer program the authors calculated the mechanical fracture energy of a 3D cross-linked plasticized elastomer filled with multifractional silica. It is of practical interest for asphalt road covering as it greatly increases the service life of road pavements.

THE THEORY OF CALCULATING THE MECHANICAL FRACTURE ENERGY

Mechanical characteristics of polymeric composite materials (PCMs) based on the 3D cross-linked plasticized elastomeric matrix filled with solid silica particles significantly affect the service life of these materials. In this regard, the most important formulation (structural) parameters are the molecular structure of the polymeric matrix of the binder, its type and degree of plasticization, maximum volume filling, depending on the shape and fractional composition of dispersed filler particles, as well as the physical and chemical interaction at the binder-filler interface [5]. Direct and indirect optimization problems of developing new types of similar PCMs with the desired combination of stress-strain properties can be solved by means of a structural-mechanical dependence which was obtained earlier [6, 7].

Let us explore a variant of maintaining the integrity of PCM until the sample breaks (Poisson's ratio → 0.5), which is of the most practical interest for increasing its service life, including working conditions of the rocket engine charge under domestic pressure.

Earlier, in connection with PCMs, we presented a physical and mathematical description of the dependence of relative (related to the initial cross-section) stress (σ (MPa)) from stretch at break (αb(mm)) of the filled elastomer with account for its basic structural parameters [7]:

$$\sigma = \nu_{ch}\,\varphi_r^{1/3}\,RT_\infty\left\{1+29exp\left[-0.225\cdot10^{-3}\left(T-T_g\right)^2\right]\alpha^{-1}a_{\dot\alpha}^{-1}\right\}\times\left(1+1.25\frac{\varphi/\varphi_m}{1-\varphi/\varphi_m}\right)^2\left(\alpha-\alpha^2\right) \qquad (1)$$

where $\nu_{ch}(mol\,/cm^3)=\dfrac{\rho}{M_c}$ is the concentration of transverse chemical bonds in the polymer binder matrix; ϱ (g/cm^3) –

density of the polymer binder; $\overline{M_c}$ – average internodal molecular weight of the 3D cross-linked polymer; φ_r (*vol. fraction*) $=(1-\varphi_{sw})$ – polymer volume fraction in the binder; φ_{sw} (*vol. fraction*) – plasticizer volume fraction in the binder; R (J/K·mol) – universal gas constant; T_∞ (K) – equilibrium temperature, at which intermolecular interaction (the concentration of transverse physical bonds – $v_{ph}(mol/cm^3)$) in the binder is negligible (v_{ph} $(mol/cm^3)\to 0$); T (K)– sample test temperature; T_g (K)– structural glass-transition temperature of the polymer binder; $a_{\dot\alpha}$ (c^{-1}) – velocity shift ratio; φ (*vol. fraction*) – volume fraction of the dispersed filler; φ_m (*vol. fraction*) – maximum permissible volume filler fraction depending on the shape and fractional composition of the filler particles.

In practice, we can estimate the structural parameter value $\bar{M}_c$ by means of a molecular graph [7]:

$$\left[\bar{M}_c\right]_\infty=\left[\left(-f_{32}\right)_2-R_3-f_{32}-R_2-f_{21}-\left(R_1-f_{12}-R_2\right)_n-f_{23}-R_3-\left(f_{32}-\right)_2\right]_\infty$$

where R_1 and R_2 are molecular chains of two rubber substances with two kinds of reactive end groups f_1 and f_2; R_3 – a molecule of the cross-linking agent with three antipodal reactive groups – f_3; combinations of subscripts at f denote the chemical reaction products of *i-th* and *j-th* antipodal reactive end groups of R_1-type and R_2-type bifunctional polymers, as well as R3-type cross-linking trifunctional agent.

Taking into account that usually $R_3 << R_1$ and R_2, we can assume that $\bar{M}_c$ is proportional to increment addition of the molar fraction of linear polymerization $-\left(R_1-f_{12}-R_2\right)_n$ according to the molecular graph.

The value of φ_m (*vol. fraction*) can be calculated [8] or determined by a viscosimetric method [9]. Relative elongation (*a* (mm)) is connected with deformation (ε (%)) by a well-known ratio rating: *a = 1 + ε / 100*. On conditions that the integrity of the material is maintained, true stress *(σ_{ver} (MPa))* is equal to the product of *σ·a*, but in practice it is more convenient to use conventional stress for comparison with research results of PCMs that do not remain integral until the sample breaks [7]. On the basis of the Eq. (1) we can write the following relation:

$$W=\int_1^{\alpha_b}\sigma\left(\alpha\right)d\alpha=\int_1^{\alpha_b}\nu_{ch}\,\varphi_r^{1/3}\,RT_\infty\left\{1+29exp\left[-0.225\cdot10^{-3}\left(T-T_g\right)^2\right]\alpha^{-1}a_{\dot\alpha}^{-1}\right\}\times\left(1+1.25\frac{\varphi/\varphi_m}{1-\varphi/\varphi_m}\right)^2\left(\alpha-\alpha^2\right) \quad (2)$$

where *W (J),*is energy (work) of mechanical fracture at uniaxial tension with dimensions: *MPa × elongation (mm) = 1·10³ J*. The latter are the equivalent of the time during which the polymeric composite material resists increasing tensile stress.

Considering W $(J,)$ and a (mm) to be variable and denoting the combination of the rest alphabetic and digital characters as constants C_1 and C_2 from the expression (2) we get the following:

$$C_1 = \nu_{ch} \varphi_r^{1/3} RT_\infty \left[1 + 1.25 \frac{\varphi/\varphi_m}{1 - \varphi/\varphi_m} \right]^2$$

$$C_2 = 29 exp\left[-0.225 \cdot 10^{-3} \left(T - T_g \right)^2 \right] a_{\dot\alpha}^{-1}$$

which allows us to write the dependence (2) in compact form:

$$W = \int_1^{\alpha_b} C_1 \left(1 + C_2 \alpha^{-1} \right) \left(\alpha - \alpha^{-2} d\alpha \right) \tag{3}$$

The Eq. (3) can be solved by means of Table of Standard Integrals [10]:

$$W = \int_1^{\alpha_b} C_1 \alpha \, d\alpha + \int_1^{\alpha_b} C_1 C_2 \, d\alpha - \int_1^{\alpha_b} C_1 \alpha^{-2} \, d\alpha - \int_1^{\alpha_b} C_1 C_2 \alpha^{-3} \, d\alpha$$

Further, as a result of integration and algebraic transformations, we obtain the equation:

$$W = C_1 \left(\frac{\alpha_b^3 - 3\alpha_b + 2}{2\alpha_b} \right) + C_1 C_2 \left(\frac{2\alpha_b^3 - 3\alpha_b^2 + 1}{2\alpha_b^2} \right) \tag{4}$$

which leads, using the notations in (2), to the required dependence of the mechanical fracture energy of PCM on its basic formulation parameters:

$$W = \nu_{ch} \varphi_r^{1/3} RT_\infty \left(1 + 1.25 \frac{\varphi/\varphi_m}{1 - \varphi/\varphi_m} \right)^2 \left\{ \left(\frac{\alpha_b^3 - 3\alpha_b + 2}{2\alpha_b} \right) + 29 \exp \times \left[-0.225 \cdot 10^3 \left(T - T_g \right)^2 \right] a_{\dot\alpha}^{-1} \left(\frac{2\alpha_b^3 - 3\alpha_b^2 + 1}{2} \right) \right\} \tag{5}$$

Let us note that the mechanical fracture energy (W (J)), is equal to zero when $a_b = 1$, indicating at its required normability.

ULTIMATE ELONGATION AND ENERGY TO BREAK

Ultimate values of relative elongation (α_b(mm)), as well as strain (ε_b(%)), can be estimated by considering the velocity and degree of strain of an average polymeric binder layer between the solid particles of the filler [7]:

$$\dot{a}_f = \dot{a}_0 \left(1 - \sqrt[3]{\frac{\varphi}{\varphi_m}} \right) + \sqrt[3]{\frac{\varphi}{\varphi_m}}$$

$$\alpha_b^f = \alpha_b^0 \left(1 - \sqrt[3]{\frac{\varphi}{\varphi_m}} \right) + \sqrt[3]{\frac{\varphi}{\varphi_m}} \tag{6}$$

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

where the indices «*f*» and ″0″ refer to the filled and free states of the 3D cross-linked plasticized polymer binder of PCM. For engineering use of the Eq. (5) when developing new PCMs based on 3D cross-linked plasticized elastomers it is necessary to know the value of the maximum relative elongation or ruptural deformation of the polymeric binder.

As follows from the relation (1), the values of α_b^0 (*mm*) or ε_b^0 (%) are determined by the polymer volume fraction in the plasticized binder (φ_r (*vol. fraction*)), effective concentration of transverse bonds (ν_{eff} (*mol/cm³*)), comprising permanent

transverse chemical bonds (v_{ch} (mol/cm³)) and variable physical (intermolecular) bonds (v_{ph} (mol/cm³)), and the latter determine the temperature-velocity dependence of the mechanical characteristics:

$$v_{eff} = v_{ch}\,\varphi_r^{1/3}\left[1 + v_{ph}\left(T - T_g\right)\right] == v_{ch}\,\varphi_r^{1/3}\left\{1 + 29exp\left[-0.225\cdot10^{-3}\left(T - T_g\right)^2\right]\right\} \tag{7}$$

The molecular structure parameter (the statistically average internodal molecular weight ($\bar{M}_c$) of 3D cross-linked systems based on low-molecular-weight polymers with terminal functional groups) was theoretically evaluated in the following paper [11]. However, the authors did not consider the molecular interaction, which as well as the mechanical properties depend, as was noted above, on a variety of factors [12-14]. Therefore, for use in engineering practice of determining the ruptural deformation of the free polymeric binder depending on the amount of v_{eff} we have summarized the experimental data obtained earlier [7].

It turned out that the nonlinear experimental dependence

$$\varepsilon_b^0\left(\%\right) = f\left(v_{eff}\right)$$

for various polymeric binders, built on a logarithmic scale [7], is linearized in the coordinates:

$$\log \varepsilon_b^0 = \log \varepsilon_b^0\,|_{\bar{M}_c\to\infty} - C\sqrt{v_{eff}} \tag{8}$$

where $\log \varepsilon_b^0\,|_{\bar{M}_c\to\infty} = 3.1$ corresponds to $\varepsilon_b^0\,|_{\bar{M}_c\to\infty} = 1250\%$; coefficient $C = 40$;

$v_{eff} \approx d/\bar{M}_c^{-1}$ is in accordance with the formula (7). After algebraic transformations we obtain an empirical dependence:

$$\varepsilon_b^0 = 10^{3.1-40\sqrt{v_{eff}}} \tag{9}$$

MATERIAL AND METHODS

Breaking strain was measured on a tensile testing machine brand "Instron," at a rate of expansion "."The materials used in the study cross-linked elastomers based on viscous-flow low-molecular rubbers with terminal functional groups – poly(butyl formal sulfide), poly(ester urethane)hydroxide, polydiene epoxy urethane, poly(isoprene–butyl), carboxyl-terminated polybutadiene – cured by three functional agents with antipodal functional groups.

Low-molecular rubbers (PDI-3B grade polydiene epoxy urethane with epoxy end groups and SKD-KTR grade carboxyl-terminated polybutadiene) were used as the polymer matrix. 3D cross-linking was performed using EET-1 grade epoxy resin.

Mixtures of silica fractions with an average particle size (600 μm, 15 μm, and 1 μm) were used as the filler.

The polymeric binder contained dibutyl phthalate as a plasticizer $[\varphi_{sw} = (1 - \varphi_r) = 0.3]$. Optimum values of the fraction parameters are listed in Tab. 1, 2 and 3. The selected standard relative strain rate is $1.4\cdot10^{-3}$ c^{-1}.

Fig. 1 presents a generalized dependence of ruptural deformation of different polymer binders (on a logarithmic scale) on the square root of the effective concentration of transverse bonds (on a linear scale).

Taking into account the relations (6), by means of the generalized dependence (9) we can determine elongation at break (α_b^0 (mm)) of the polymeric binder in the free state and hence the ultimate elongation of the three-dimensionally cross-linked filled elastomer (α_b^f (mm)), which allows us to calculate the energy of its mechanical fracture at uniaxial tension.

The Eq. (5), showing the dependence of fracture energy on the parameter φ / φ_m, was applied for a PCM based on a low-molecular rubber.

Fraction number	Particle diameter, μm	Pore volume ratio	Optimum values of fraction volume ratio	Maximum volume filling
1	15	0.386	0.2	
2	600	0.244	0.8	0.84

Table 1: Parameter values of mixtures of two silica fractions

Fraction number	Particle diameter, μm	Pore volume ratio	Optimum fraction volume ratio	Maximum volume filling
1	1	0.465	0.05	
2	15	0.386	0.149	0.94
3	600	0.244	0.801	

Table 2: Parameter values of mixtures of three silica fractions.

Fraction number	Particle diameter, μm	Pore volume ratio	Optimum fraction volume ratio	Maximum volume filling
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 3: Parameter values of mixtures of four silica fractions.

Fraction quantity, piece	2, 3, 4
Experiment temperatures, *K*	223, 273, 323
Polymer glass transition temperature, *K*	175
Plasticizer glass transition temperature, *K*	185
Polymer volume-expansion coefficient	$5 \cdot 10^{-4}$
Plasticizer volume-expansion coefficient	$7 \cdot 10^{-4}$
Volume fraction of the polymer in the binder	0.25
Glass transition temperature of the composite elasomer, *K*	177
Filler volume ratio in mixed solid rocket propellants	0.75
Chemical bond concentration in the binder, *mol/cm³*	$1 \cdot 10^{-5}$
Maximum filler volume ratio	0.84; 0.94; 0.96

Table 4: Initial data for calculating the mechanical fracture energy.

For comparison, we considered composite materials based on polymeric binders with mixtures of two, three and four (Fig. 2) silica fractions.

It is seen that, contrary to Smith failure envelopes [1-4] and [17], the mechanical fracture energy reflects the mechanical resistance of PCM as a filled elastomer more fully in the physical sense, which is important when estimating its operational suitability in particular materials.

The dependencies in Fig. 2 allow to evaluate the influence of the quantity of fractions taken in the optimal ratio, on the amount of ruptural deformation (the value of the mechanical fracture energy being practically constant).

For example, at the temperature of 223 *K* ε_b (%) changes from 0 to 16% (2-fractional silica), from 0 to 25% (3-fractional silica), from 0 to 35% (4-fractional silica), which, respectively, leads to a double increase of ε_b.

A similar phenomenon is observed at temperatures of 273 *K* and 323 *K*.

The latter circumstance is very favorable for the use of PCM as frost and waterproof asphalt coating of automobile roads.

It is important to add that the increase of ruptural deformation of PCM as 3D cross-linked filled plasticized elastomer in accordance with the Eq. (1) is contributed by the decrease in the values of other structural parameters – $v_{ch}, \varphi_r, \varphi / \varphi_m$, –

as well as the structural glass-transition temperature of the polymer binder. In this case, the decrease in ultimate tensile stress (σ_b (*MPa*)), related to (a_b (*mm*)) by the formula:

$$\sigma_b = C_1\left(1 + C_2\alpha_b^{-1}\right)\left(\alpha_b - \alpha_b^{-2}\right)$$

with previously adopted notations applied to the Eq. (1), occurs to a lesser degree. This can probably explain the corresponding increase in the values of *W* (*J*), at increasing ε_b(%). The theoretically derived dependence (5) of the mechanical fracture energy of a 3D cross-linked filled elastomer from the basic structural parameters of the composite can be recommended for solving direct and indirect problems when developing new PCMs as polymer composites for various purposes with the desired combination of performance characteristics [7]. In doing so, it is expedient to use computer programs, including mathematical optimization techniques [15, 16], which will help to reduce the development time and cost of raw materials, for example, when developing advanced PCMs.
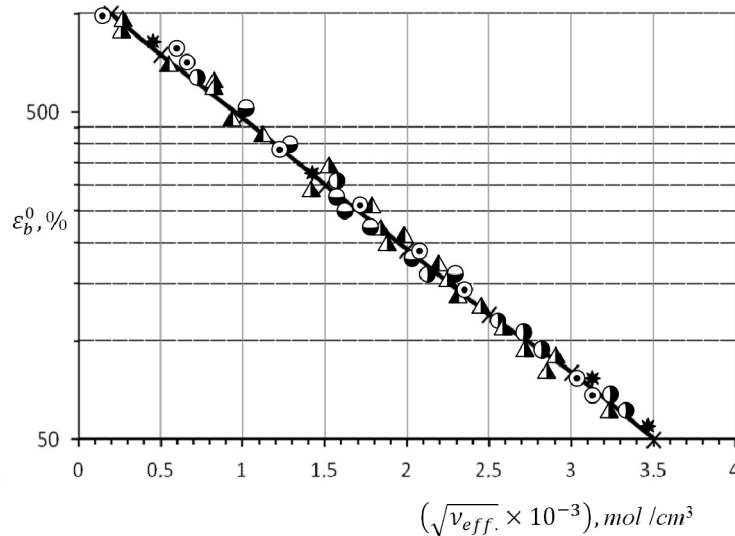

Figure 1: Experimental dependence $\varepsilon_b^0\left(\%\right) = f[\left(\nu_{eff}\right)mol/cm^3]$ for various polymeric binders based on:

▲: Poly(butyl formal sulfide), ▲: Poly(ester urethane) hydroxide, ☉: Polydiene epoxy urethane, ✸: Carboxyl-terminated polybutadiene, ◑: Polyisoprene butyl; The data are given for standard conditions: *T*=293 *K* and $\dot{\alpha}$ =1.4·10⁻³ *ċ⁻¹*.
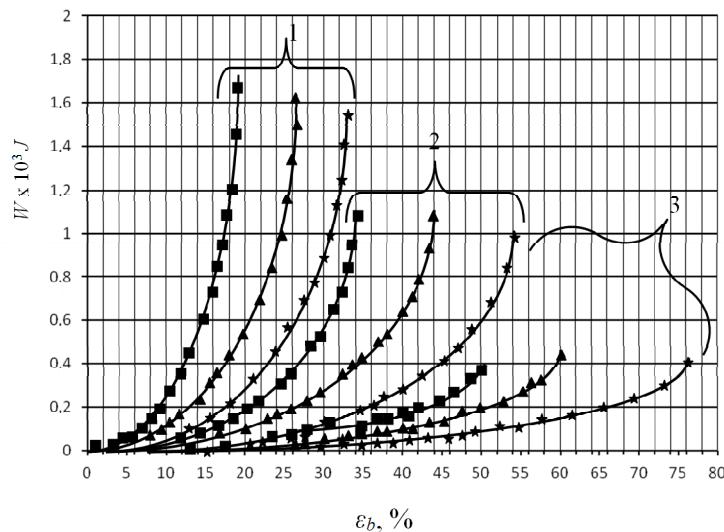

Figure 2: Dependence of the mechanical fracture energy on ruptural deformation of a PCM at temperatures: 1 – 223 *K*; 2 – 273 K; 3 – 323 K. ■: two-fraction composition; ▲: three-fraction composition; ★: four-fraction composition;

CONCLUSION

The article presented the equation linking the mechanical fracture energy of the 3D cross-linked polymer binder filled with multifractional silica and its basic formulation parameters.

The authors proposed a generalized dependence of ruptural deformation of the polymer binder from the effective concentration of chemical and physical (intermolecular) bonds for calculating the mechanical fracture energy of new PCMs.

It has been shown that the increase in the quantity of fractions of solid components taken in the optimum ratio leads to a double increase of ruptural deformation at constant mechanical fracture energy.

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