Scale effects in tribological properties of solid-lubricating composites made of ultra-high molecular weight polyethylene filled with calcium stearate particles

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Abstract. Friction properties being influenced by scale effects are simulated in the paper by the example of polymer composite material made from Ultra High-Molecular Weight Polyethylenes (UHMWPE) filled by calcium stearate ($C_{36}H_{70}CaO_4$). Of interest are the composites whose mechanical properties and tribotechnical characteristics do not depend monotonically on filler (inclusions) weight fraction. In order to describe the influence of scale effects onto frictional properties the model based on Reiss averaging (model of "weak phase") is employed. It is also suggested that when gradient elasticity theory is applicable the formal analogy between effective friction coefficient for surface heterogeneous structures and effective mechanical properties (compliances) for heterogeneous material can take place. Theoretical dependence to describe nonmonotonic change of effective friction coefficient versus filler concentration was obtained for the polymer composites under study. The suggested expressions might be useful for the sake of properties prognosis of antifriction polymeric materilas.

1. Introduction

Composite materials made from Ultra High-Molecular Weight Polyethylene (UHMWPE) obey numerous significant properties including low density, unique ability to absorb shock impacts, chemical and biological inertness, satisfactory strength properties, high wear resistance etc. [1]. Due to their unique properties such composites are of wide demand in mechanical engineering, medicine; they might be as well used at design of engineering structures in oil and gas engineering, mining, power and chemical engineering, etc. High stability of properties within certain temperature range and extremely low friction coefficient [2-6] make these materials very attractive for design of machine parts and equipment to be exploited under extreme conditions of Arctic climate. Particularly, this is related to antifrictional materials.

Numerous papers indicate that in many polymeric composites modified by micro- and nanosized inclusions nonmonotonic dependencies of physical-mechanical properties on filler concentration take

place [7,8]. Particularly, according to [8], dependencies of this kind are characteristic feature for strength and tribological properties of modified polymers. Apparently, these nonmonotonic dependencies are related to manifestation of scale effects known for composites of different types.

This paper deals with the development of a model to estimate frictional properties of modified polymers which takes into account scale effects. The ultimate aim of the model is calculation of exploitation properties based on data of filler content that might by supported by the experimental data taken from the literature. It is worth noting that experimentally determined mechanical characteristics such as strength, hardness, etc. as well point at their abnormal nonmonotonic behavior with increase of filler concentration.

2. Modeling of effective friction coefficient

Let us consider that the polymer is modified by inclusions made from calcium stearate with characteristic dimension of r_0 and volume concentration c. The relation between the relative part of inclusion surface and volume concentration is determined by the formulae $S_{slip} = K c^{2/3}$, where coefficient K is determined by the packing density and shape of the filler particles. For dense packing of spherical particles, the coefficient K can be calculated explicitly and was evaluated to take the value of $K_0 \approx 1.268$. However, the change of shape and surface roughness of the particles is not taken into account. For the case of arbitrary shape of the particles this parameter can be much higher than K_0, but the condition $K c^{2/3} < 1$ should be true.

For the friction coefficient evaluation it is suggested to use the model being based on the analogy with the "weak link" one where the effective properties of lamellar or nonuniform structures at the serial arrangement of phases are determined (limited) by a weak link. It might be assumed that for the parameters being inverse to the friction coefficient the mixture rule is true that is analogously to the mixture formula for compliances calculation of nonuniform composites in a one dimensional approximation. Though the direct calculations show that above mentioned formula for the effective friction coefficient does not taken into account scale effects and gives monotonic dependence on concentration that does not correspond to experimental data.

At the use of this model the averaged value of friction coefficient does not depend on the modification parameter, i.e. the scale factor (specific size of the inclusions or, that is here the same, on the extent of interphase layer) that naturally appear when mechanical properties are modeled being based on the gradient model. To take into consideration the influence of the scale effect let us continue the above introduced analogy between coefficients of friction and compliance in a heterogeneous composite with micro/nano scale structure. The estimations of mechanical properties for nanocomposites with regard to scale effects were obtained previously in [9,10].

In gradient theory of elasticity, scale factors are determined by the thickness of the interphase zone as well as by the parameter A representing the activity of inclusion surface affecting the crystallization zone of the polymer in the vicinity of calcium stearate particles. As the basic the following formula to evaluate the effective stiffness of lamellar periodic structure will be used [10]

$$k = \frac{k_M H_M L + k_I H_I l}{L + l} = \frac{k_M k_I (k_I \alpha_M + k_M \alpha_I - A_{st}\, \alpha_I \alpha_M)}{Q}(L + l),\qquad(1)$$

where l is the thickness of inclusion layer, $L = l(1-c)/c$,

$$H_M = k_I \frac{k_I \alpha_M + k_M \alpha_I - A_{st}\, \alpha_I \alpha_M}{Q}(L+l),\quad H_I = k_M \frac{k_I \alpha_M + k_M \alpha_I - A_{st}\, \alpha_I \alpha_M}{Q}(L+l),$$

$$Q = (k_I L + k_M l + A_{st})(k_I \alpha_M + k_M \alpha_I - A_{st}\alpha_I \alpha_M) - (k_I - k_M - A_{st}\alpha_I)(k_I - k_M + A_{st}\alpha_M),$$

$$\alpha_M = \frac{\kappa_M}{\text{th}(\kappa_M L)}, \quad \alpha_I = \frac{\kappa_I}{\text{th}(\kappa_I l)}, \quad k_{I,M} = 2\mu_{I,M} + \lambda_{I,M}, \quad \kappa_{I,M} = \sqrt{C_{I,M}/k_{I,M}}.$$

Here c is the volume part of inclusions in the representative fragment; $\hat{l}_{I,M} = (\kappa_{I,M})^{-1}$ is relative thickness of interphase layer in each fragment phase; A_{st} is the surface activity parameter. It is suggested that A_{st} parameter affect the structure of crystallization zone and its stiffness.

Note that relation (10) were obtained in [10] in accordance with the procedure of the asymptotic averaging being generalized for gradient model.

Using the averaging procedure for the values being inverse to friction coefficient and taking into account the formula (1) the following expression for effective friction coefficient can be written:

$$\overline{k} = (1 - S_{slip}) + S_{slip}\left(\overline{k}_{slip}(1 + \hat{A}_{slip}) - \frac{\left(1 - \overline{k}_{slip}(1 + \hat{A}_{slip}\alpha_I)\right)\left(1 - \overline{k}_{slip}(1 - \hat{A}_{slip}\alpha_M)\right)}{\alpha_I \overline{k}_{slip}(1 - \hat{A}_{slip}\alpha_M) + \alpha_M}\right), \quad \hat{A}_{slip} = \frac{A_{st}}{r_0}. \quad (2)$$

Thus, in gradient model of tribology the effective friction coefficient is determined by a number of parameters. Among them are, effective coefficient K that determines the packaging and geometrical shape of particles to fill the matrix; $\hat{l}_{I,M}$ - the relative thickness of the interphase zone in a matrix and in an inclusion; $\hat{A}_{slip}$ - parameter of surface activity for inclusions that accounts for the influence of the excess free energy on the crystalline structure formation on the surface of the phases.

Note that excess free surface energy was included as a thermodynamic parameter (additional generalized thermodynamic force) in the classical thermodynamics [11,12] of surface effects and phase equilibriums as well as in thermodynamics of a media with internal surfaces [13,14] which are described using additional parameter – specific surface area. In doing so, these values are thermodynamic state variables.

After fitting the parameters to provide the best approximation of experimental data [8] there was obtained the following results: $\overline{k}_{slip} = 0.29$, $K = 3$, $\hat{A}_{slip} = 10$. Parameter of interphase zone thickness in the matrix $\hat{l}_M = l_M / r_0$ (it is assumed that $\hat{l}_I = 0$) and its dependence on inclusion concentration are adjusted during the modeling of effective properties of the filled polymer; here r_0 is effective radius of particles with regard to cluster formation. Theoretical estimations for effective mechanical properties (strength) of filled composite were obtained in [9] based on gradient elasticity theory and method of radial factors. It was ascertained that for the composites under study the dependence $\hat{l}_M = a/(b+c) - d$ can be used when $c \in [0,9]$ and $c \in [9,20]$. The parameters a, b, d were determined through the condition of the best agreement of experimental data [8] and data of the ultimate strength modeling. Following values were found [8]: $a = 3.221$, $b = 0.363$, $d = 6.887$ for $c \in [0,9]$; and $a = 0.00327$, $b = -0.0756$, $d = 0$ for $c \in [9,20]$. In doing so, the tribology model tends to be related to the strength model for the composite.

The graph for theoretical dependence (2) of effective friction coefficient on volume content of inclusions is presented in the fig. 1 (curve 1); solid dots on the graph correspond to experimental data. Curve 2 corresponds to effective friction coefficient being calculated in accordance with the mixture rule $\overline{k} = (1 - S_{slip}) + S_{slip}\overline{k}_{slip}$.
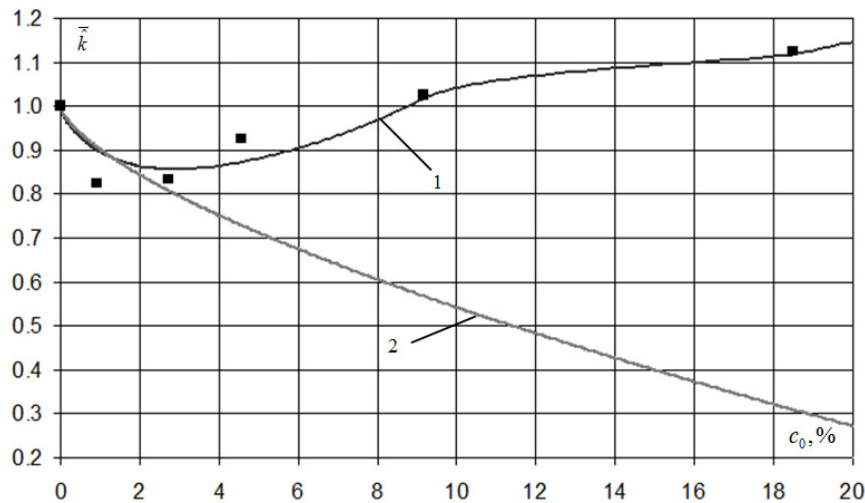
Figure 1. Effective friction coefficient calculated by gradient model of tribology; dots – experimental data; line 1 – corresponds to gradient model; line 2 – corresponds to classical approach.

3. Conclusion

The model for calculating friction properties of modified high molecular weight polymers is offered. It was established that there is a certain analogy between the model of mechanical properties and friction model since scale effects for friction coefficients are taken into account based on the dependence of the interphase layer thickness (the thickness of crystallization zone) on filler concentration that was found during mechanical properties modeling. It was demonstrated that the suggestion on the analogy between friction coefficient and compliance is quite correct. Using this analogy the method of friction properties (friction coefficient) evaluation was suggested for heterogeneous polymeric structures taking into account the nonmonotonic dependence of these characteristics on the concentration of the modifying filler.

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