Energetic self-organization and development of the structural scheme of a polymer fiber tribosystem

Tojiboy Almataev*, *Said Abrorhon* Yusupov, and *Nozim* Almataev

Andijan Machine-Building Institute, Andijan, Uzbekistan

Abstract. The article presents the results of the analysis of the main processes of friction of polymeric materials during friction with fibrous mass from the standpoint of irreversible processes and developed a block diagram of a polymer fiber tribosystem.

1 Introduction

During the frictional interaction of materials, various interrelated physical, physicochemical processes occur, which caused the emergence of various hypotheses and theories of external friction of solids; molecular-mechanical, atomic-molecular, mechanical-chemical theory of friction, structural adaptability, etc.

An analysis of the development of modern studies of tribology shows [1-9] that it consists in considering microscopically observed patterns as a result of the manifestation of microscopic processes that real objects are subject to. This trend has led to the formation and development of energy concepts in the evaluation of frictional interaction processes, in which the energy characteristics of the process are associated with the characteristics of changes in the structure of friction surfaces [1–7].

Further development of energy concepts was possible using the fundamental laws of thermodynamics.

2 Methods of research

The energy properties of polymeric materials and coatings based on them are determined on an improved tribometer, for which a patent of the Republic of Uzbekistan No. 1989 was obtained. Methods for studying the thermodynamic processes of open systems were applied.

3 Results and discussion

The essence of applying the laws of classical thermodynamics to non-equilibrium systems lies in the assumption of local equilibrium within small elements of the system regions.

*Corresponding author: iscmmstiai2022@gmail.com

This idea of local equilibrium makes it possible to study a large number of nonequilibrium systems, which include the tribo-system. For example, the Gibbs equation, which shows the dependence of the internal energy U on the entropy S, volume V, and chemical potentials μ_k of the system components, is written [1] for any region in the form of:

$$dU = TdS - pdV + \sum \mu_k \cdot dC_k$$

where numerical U, S, V - refer to a small area, C_k - concentration of components.

In this case, the calculation of local values of internal energy (entropy) has difficulties, but it can be overcome by applying the principle of calculation using entropy balance equations [2].

$$p\frac{dS}{dt} + \operatorname{div} S = G[S] \qquad (1)$$

Here: pdS/dt - entropy growth rate in the given area; div S - rate of outflow of entropy from a given area; G [S] - the rate of occurrence (production) of entropy within the region.

B.I.Kostetsky, referring to the tribo-system to open thermodynamic systems exchanging energy and matter with the environment, believes that the essence of structural and energy adaptability is that with normal friction in the contact zone, dissipative structures are formed that have the property of minimal entropy production [3]. In [4], the author, analyzing the process of self-organization of metal-polymer tribo-systems, shows that during frictional interaction, a dissipative inhomogeneity of the determining parameters, such as temperature gradients, dislocation density, concentration, and electrochemical potential, arises in the system.

N.M. Klementyev [5] proposed the equation of thermodynamic friction to describe the thermal thermodynamic process:

$$F_1 dl - F_2 dl = dU_1 + dU_2 + dU_3 + \ldots + dU_n$$

In [6], the author concluded that with a constant energy flow in the system and a constant temperature, the rate of entropy generation dS/dt is determined only by the properties of the system, its thermal resistance. It is not suitable for the analysis of the state of the tribo-system, since it does not take into account the influence of the exchange of energy and matter with the environment, the energy of chemical reactions, and triboelectric effects on the rate of production of entropy and the state of the tribo-system.

To solve the problem of optimizing tribo-systems that implement the phenomenon of selective transfer during friction, the work [7, 8] uses the mathematical apparatus and principles of non-equilibrium thermodynamics. The Gibbs equation is written in local form for each region and, assuming that the total energy is conserved, the total entropy differential is obtained in the form:

$$TdS_{\sum} = a_v \Delta \tau dE_i - \Delta \mu dn_i$$

where: E_i, n_i - plastic deformation and concentration of particles of the same type in the $i-$ th local equilibrium region.

However, it is very difficult to measure the plastic strain rate $\boldsymbol{\varepsilon}$ during friction, so the authors propose to take the friction coefficient f as a thermodynamic flow, but replacing ε by f leads to a significant coarsening of the model.

An analysis of the above works and other theories allows us to conclude that physically justified generalizations and models should be based on the fundamental laws of thermodynamics.

Based on the laws of non-equilibrium thermodynamics, we have attempted to describe the mechanism of structural-energy self-organization of a polymer-fiber tribo-system.

From the point of view of thermodynamics of irreversible processes, a polymer-fiber tribo-system is an open non-equilibrium thermodynamic system, since non-equilibrium heat transfer and diffusion processes occur during thorns, which are the result of differences in the values of thermodynamic forces, such as temperature, pressure and concentration. Consequently, these thermodynamic forces are gradients that characterize the remoteness of the tribo-system from thermodynamic equilibrium.

Let us consider the main physical-mechano-chemical processes during the friction of fibrous materials on a polymeric counter-body.

Our studies have shown that all pathological changes in structural and energy parameters occur in the initial period of friction, i.e., during the period of unsteady friction [8-10]. At the end of the period of non-stationary friction of polymer-fiber mass pairs, new, more stable structures and energy parameters are formed, which differ from the original ones and depend on the type, material properties, friction mode, and conditions.

During the friction of polymeric materials with fibrous mass, in contrast to the friction of solid bodies, the process of frictional interaction is accompanied by the formation and accumulation of a large amount of heat, and an increase in the triboelectric charge density (energy parameters).

Experimental studies have established (Fig-1) that the energy parameters of the pairs of polymer-fibrous mass in the initial period of friction increase monotonically and stabilize after a while. Fig. 1 shows that at the value of the factor PV=0.04 MPa* m/s, the temperature in the friction zone and the density of the tribo-charge first increase intensively, then reaching the maximum value, it stabilizes. The time at which the value of the studied parameters reaches stable values depends on the type and properties of the polymer. Stabilization of the value of the steady temperature is observed when the tribo-charge density has a constant value. With an increase in the factor P V, the maximum of the steady-state temperature shifts towards a decrease in the period of unsteady friction. Moreover, the absolute value of the energy parameters of the run-in and unrun surfaces are different. This indicates that a spontaneous phase transition occurs in the system; the process of self-organization of the system.

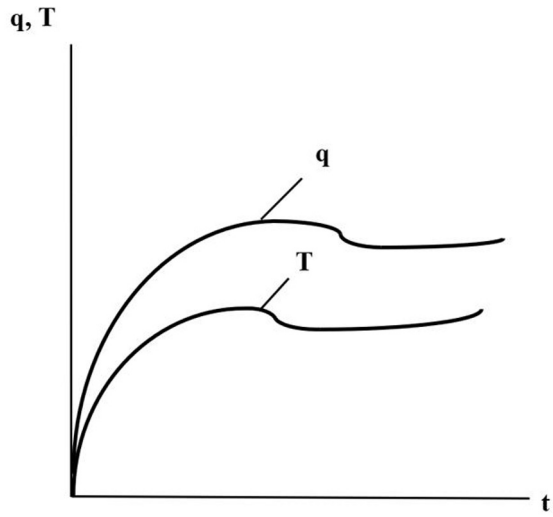

Fig. 1. Change in the energy parameters of the polymer-fiber tribo-system

An analysis of the process of self-organization of polymer-fiber tribo-systems shows that when moving in the system, a dissipative inhomogeneity of the determining parameters arises, for example, temperature gradients, electrostatic forces, etc. After setting the values of temperature in the friction zone and tribo-charge density, the friction process stabilizes, which is characterized by an average value of friction forces and intensity wear. Under such friction conditions, the dissipation of thermal energy is also characterized by a certain average, approximately constant, which indicates the constancy of the average values of energy flows in the system and its stationary thermodynamic state.

The results of our studies allow us to conclude that during the period of non-stationary friction of polymer-fiber tribo-systems, the first stage of self-organization of polymer materials is realized. It is characterized by the formation of dynamic anisotropic tribo-structures under the conditions of thermomechanical friction, which provide a significant reduction in the activation energy of the viscous flow. This dissipative phase transition of the system from an initial unstable equilibrium state to a stable metastable state is accompanied by a change in the Gibbs free energy for each small volume element due to a decrease in entropy. If considered from the position of structural-energy self-organization, then this stage is characterized by intensive destruction of equilibrium structures and the emergence of new tribo-structures with higher antifriction properties. In the process of unsteady friction at a certain critical value of the energy flow-entropy of the external action (loading-pressure and sliding velocity, medium-humidity) new, dissipative stable structures arise.

However, these structures containing, for example, free radicals or wear products, are unstable. Therefore, a transition to a new, more stable state is inevitably made with the formation of energetically advantageous dissipative tribological structures.If we schematically represent the tribo-system in the form of a model (Fig. 2) with two energy levels U_1 and U_2, then the level U_1 will characterize the energy "friction barrier" of the contacting initial equilibrium structures (run-in). The system goes into a more stable state with energy level U_2 as a result of the formation of winning dissipative tribo-structures with higher antifriction properties (normal friction).

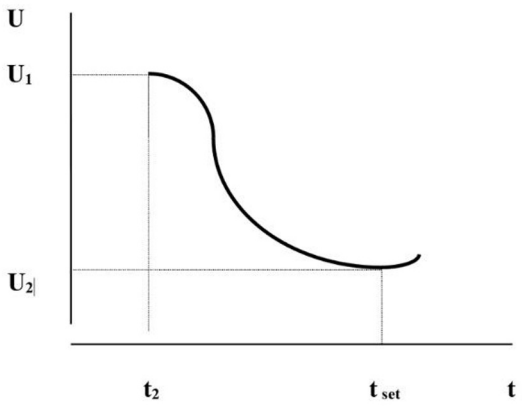

Fig. 2. Scheme of changing the friction energy barrier

According to the Glensdorf-Prigogine theory of the creation of structures, the emergence of dissipative tribo-structures can be considered the result of the instability of the tribo-system in the transition process, the exchange of energy and matter with the environment. The measure of the rate of formation of dissipative tribo-structures is the production of excess entropy. The appearance of such tribo-structures contributes to the

transition of the system to a stationary state when the thermodynamic forces (temperature in the friction zone and triboelectricity charges) become constant. This is confirmed by the results of our experimental studies.

A polymer fiber tribo-system consisting of a polymer and fibrous mass will be considered as a thermodynamic system and characterized by its thermodynamic parameters and functions. To develop a thermodynamic model, let's take a part of the tribo-system, mentally separating it from the environment.

The system consists of a polymeric body -1, a fibrous body -2, an intermediate frictional transfer film -3, and is macroscopic since it consists of a large number of particles of different sizes (Fig. 3). By the nature of interaction with the environment, the tribo-system is open, since it can exchange with the environment, energy, and matter.

The tribo-system should be classified as heterogeneous since in terms of its structural composition it contains three phases, the state of which can be described by continuous functions of spatial coordinates and time.

The basis for the use of the continuous model can be the physicochemical processes considered above during friction [9–18].

To determine the structure of the future model, we consider the nature and sequence of thermodynamic processes occurring in the tribo-system during friction, for which we present them in the form of a block diagram. Tribological system experiences an external energy impact, characterized by the load P, sliding speed V and ambient temperature T (block A). The friction energy E generated by them is transferred in a certain ratio to two rubbing bodies (fibrous and polymer) of the tribo-system (blocks B_1 and B_2), the thermodynamic properties and state of which are determined by the corresponding parameters: C_{p1} and C_{p2} heat capacity; M_1 and M_2 - mass; T_1 and T_2 - temperature. The friction energy causes an increase in temperature and structural changes in the contacting volumes (in the polymer), which are aimed at reducing the ordering of the structure (decrease in the degree of crystallinity, increase in the amorphous phase of polymers), and increase in configurational entropy. These processes are accompanied by a change in the entropy of the fibrous and polymer phases of the system, which is determined by the corresponding production of excess entropy $d\theta/dt$, since at this stage of friction (during the running-in period), thermodynamic forces (for example, temperature, concentration of a part of the fillers of the polymer phase) do not remain constant. An increase in the entropy of the system and structural changes in the polymer phase associated with an increase in molecular mobility under the influence of fluctuations lead to the formation of more ordered dissipative tribo-structures (C1 and C2 blocks) from a disordered (amorphous) structure with local production of entropy, typical for this stage of friction, $dS_i/dt = \theta$ in the elementary volumes of the contacting surfaces. At this stage, the formation of a frictional transfer film with parameters Cp_3 and M_3 is completed and the system transitions to a stationary state, while part of the configurational entropy generated inside the system is dissipated in the form of a flow by the medium (blocks D_1 and D_2), the other goes to the accumulation of entropy in the frictional transfer film in wear volume (block F).

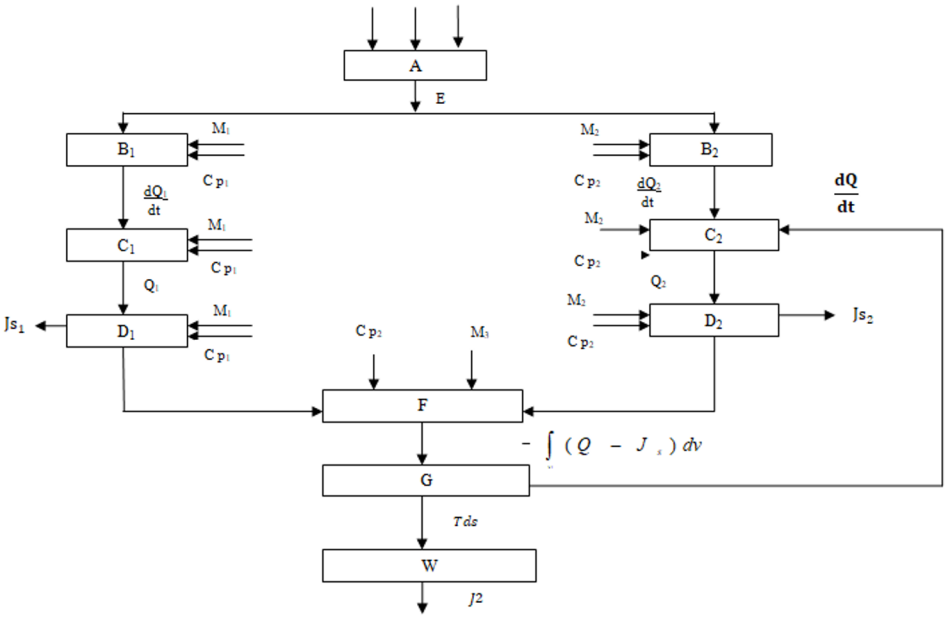

Fig. 3. Structural scheme of thermodynamic processes in a polymeric fibrous tribo-system

The appearance of dissipative tribo-structures contributes to the transition of the system to a stationary state, when the thermodynamic forces become constant, and the production of excess entropy associated with a change in thermodynamic forces is zero. The entropy $\theta = \int(\theta - J_\nabla)\,dV$,which is totally accumulated in the volume of the tribo-system is defined as the sum of the entropies of weakly interacting subsystems [1] (fibrous and polymeric) according to the additivity of thermodynamic functions (block G).It determines the degree of destruction (wear) of a less durable polymer material (block W) and, through the feedback channel, has a control effect on the formation of the entropy dissipation flow J_∇ by the environment and on the increase in entropy in the frictional transfer film (wear volume). The feedback action ensures the stability of the stationary state of the tribo-system, which is characterized by the minimum production of entropy and dissipation by its environment and, as a consequence, the minimum and constant values of the friction force and wear rate. With an increase in the friction force for any reason (for example, a consequence of the destruction and reduction in the area of dissipative tribo-structures), the temperature in the friction zone will immediately increase, which will cause a gradient of thermodynamic forces and excess entropy $d\theta/dt$(block G). Through the feedback channel, the information signal about the production of excess entropy enters block C_1 and causes an acceleration of the process of formation of dissipative tribes of structures. As a result of this acceleration, the area of dissipative tribo-structures necessary to maintain the steady state is restored, the temperature and friction force are reduced to the previous value, the production of excess entropy is reduced to zero, and the tribo-system continues to operate in a stationary mode with a minimum production of entropy. Such a transient process will be repeated every time the system deviates from the stationary state. At the same time, the return of the system to the minimum entropy production occurs due to the production of negative entropy (due to the return of configurational entropy to the environment) during the formation of dissipative tribo-structures.

From the analysis of the block diagram, which reflects the production of entropy within the tribo-system and its dissipation by the environment, it follows that in the process of frictional interfacial interaction, the total entropy of the tribo-system increases, gradually

reaching a certain critical value. In this state of the system, the internal energy in the active volumes of the friction transfer polymer film and the polymer part, equal to TS, is sufficient to destroy intermolecular and interatomic (chemical) bonds (i.e., it is greater than or equal to the destruction activation energy U_0) in these polymer phases and the formation micro- and macro defects with subsequent destruction (wear) of the polymer material in the thinnest layers.

4 Conclusions

Thus, the experimental data obtained and the analysis of physicochemical processes during friction in a polymer-fiber friction pair from the standpoint of thermodynamics leads to the conclusion that:

- in polymer fibrous tribo-systems, after the end of the running-in period with stable friction, the processes of formation of dynamic dissipative tribo-structures are continuously going on, providing a stable and minimum value of the friction forces, and the destruction of these structures, providing a stable and minimum value of the friction force, and the destruction of these tribo-structures is compensated by their restoration due to information feedback, which are channels for the transfer of energy signals;

- it became possible to develop a block diagram (physical model) of a thermodynamic (entropy-energy) model of a polymer fiber tribo-system. The use of entropy as a criterion for changing the state of a tribo-system makes it possible to theoretically take into account the effect of all physicochemical processes generated by friction on the wear rate of a polymer body and to evaluate energy losses due to friction, changes in the composition of a composite material and technology for manufacturing parts through a change in density, thermal conductivity, electrical conductivity, chemical potential and other material properties.

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