Another approach to studying friction processes

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The paper describes experiments on friction of polymers under atmospheric and vacuum conditions by using mass-spectrometry and plasma induced thermal luminescence methods. The approach is illustrated by the examples of friction of polyoxymethylene against polyoxymethylene and steel. The observed decrease in the amount of short segments of macromolecules involved in γ-relaxation observed in thermal luminescence experiments has been tentatively interpreted by variations in their conformation upon friction-induced orientation of the macromolecules in subsurface layers and rupture of macromolecular bonds.

Keywords: friction, polyoxymethylene, mass-spectrometry, thermal luminescence, molecular dynamics, polymer.

The friction energy conversion leads to various structural changes in macromolecules, for instance, to their orientation and rupture. Of great interest are the friction mechanisms of polyoxymethylene (POM) since this polymer is actively used in friction units [1]. In work [2], it was shown by the mass spectrometry method that during the POM−POM friction a friction force transition from a lower level to a higher one is observed. The transition is in straightforward correlation with the formation of decomposition products of the POM macromolecules. In this work, friction surfaces of POM in the POM−POM and steel−POM pairs obtained under the atmospheric conditions were studied by plasma induced thermal luminescence (PITL). In addition, the character of formation of the POM decomposition products in those friction pairs in the vacuum of mass spectrometer (MS) were compared.

To determine the friction parameters (friction force F_{fr}, normal load F_n, sliding speed V), we used friction machine of our own design for experiments in vacuum of $\sim 10^{-6}$ Torr in a reflectron time-of-flight MS [2] and friction machine operated in atmospheric conditions [3]. The machines operate in identical friction geometries (thrust bearing) and use the same devices [2] for recording friction force F_{fr}. The counter bodies were hollow cylinder height 18 mm, 9 mm and 6 mm outer and inner diameters rotating about its axis and a stationary plate ($\sim 2 \times 15 \times 20$ mm). The top of the cilynder is loaded on the plate. Industrial POM (POM-H, Ticona^{TM}), polytetrafluoroethylene (PTFE) (Industrial and Commercial Enterprise „Polimerkhimprom") and steel 20 (roughness $R_a \sim 0.5 \mu$m) were used. The friction-induced mass loss (Δm) of the samples was determined as a difference in the sample mass (measured by analytical balance Kern-770 with an accuracy ~ 0.1 mg) before and after friction. The TL method detects the erosion of electron traps at temperatures of relaxation transitions of polymers during heating (heating rate used

is 10 K/min) In PITL experiments the near-surface layer of few nanometers thickness is activated by plasma (power of ~ 0.4 mW/cm^3) [4,5]. For the PITL experiments with the POM−POM friction pair, the POM film (thickness of the film $\sim 100 \mu$m is predetermined by the peculiarities of PITL device) and POM cylinder were fabricated by isothermal crystallization from melt under the pressure of 10 MPa (150°C, 1 h, press Carver, USA). In the case of the steel−POM pair friction, the POM film was obtained under the same pressure by non-isothermal crystallization during cooling of POM melt to room temperature. The POM films were firmly glued onto a steel substrate. To minimize the influence of the adhesive joint mechanical properties on the contact parameters, the experiments were carried out at relatively low loads (14 N).

Fig. 1, a shows the F_{fr} dependences on time t obtained in the MS vacuum for pairs POM−POM (curve 1) and steel−POM (curve 2) at the same initial levels of F_{fr} ($F_n = 130$ N, $V = 0.021$ m/s). Dots in Fig. 1, a represent the dependences of intensities of the oxymethylene and trioxane mass-spectral peaks (their ratio remains invariable during friction); line 3 represents the dependence of the total pressure in the MS vacuum during friction in the POM−POM pair. For the POM−POM pair, the increase in the intensity of the oxymethylene and trioxane mass-spectral peaks (curve $1a$) is in straightforward correlation with the F_{fr} transition from the lower $F_{fr}^{\min}$ to the upper $F_{fr}^{\max}$ level. For the steel−POM pair, a weak smooth increase in F_{fr} and negligible (at the same MS sensitivity) variations in the intensity of the oxymethylene and trioxane peaks are observed (curve $2a$). At the end of the experiments, atmosphere was first vented into the vacuum chamber of MS to the preset total pressure (the device is equipped with an air admission needle valve) and then to the normal atmospheric pressure (see arrows at curve 3). During the air admission the short-term fluctuations in friction force F_{fr}
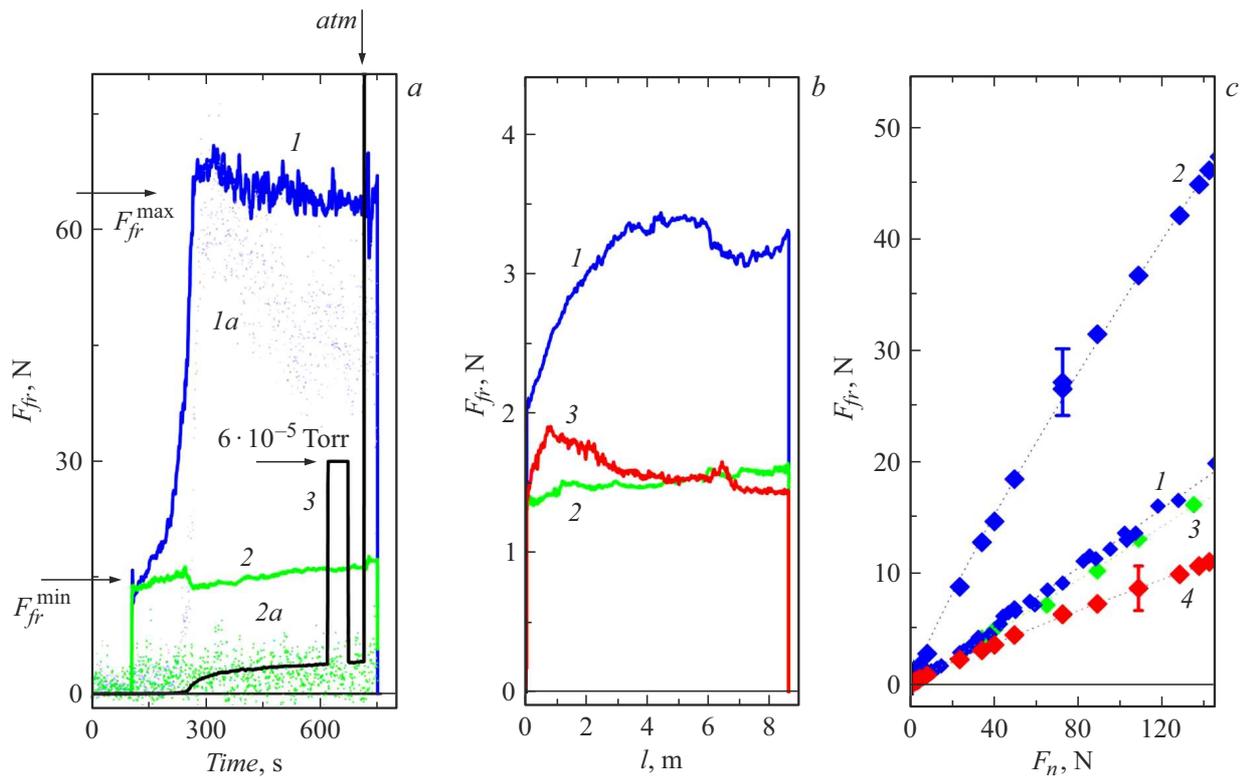
Figure 1. a — F_{fr} dependences on friction time for pairs POM–POM (line 1) and steel–POM (line 2), corresponding dependences of the rate of the oxymethylene and trioxane formation in dimensionless relative units (points $1a$ and $2a$), and dependence of the total MS chamber pressure in the course of the experiment with the POM–POM pair friction (curve 3). The pressure was measured by vacuum gauge Dual Mag972B. Magnitudes of pressure increments are height 18 mm, 9 mm and 6 mm outer and inner diameters arrows. Friction conditions: $F_n = 130$ N, mean sliding speed $V = 0.021$ m/s. Horizontal arrows indicate the lower (F_{fr}^{min}) and upper (F_{fr}^{max}) friction force levels for the POM–POM pair. b — F_{fr} dependences on the friction path for pairs POM–POM (1) and steel–POM (2) used to prepare friction surfaces studied by PITL. 3 — friction in the PTFE–PTFE pair. Friction conditions: $F_n = 14$ N, average sliding speed $V = 0.021$ m/s. c — typical F_{fr} dependences on F_{fn} for friction pairs POM–POM (1, 2), steel–POM (3) and PTFE–PPTFE (4). Dependencies 1 and 2 were plotted based on the initial (F_{fr}^{min}) and final (F_{fr}^{max}) friction force levels (see text). Friction conditions: mean sliding speed $V = 0.021$ m/s.

are observed, but the average magnitude of the friction force does not change. Recall that upon thermal decomposition of POM only oxymethylene is detected above $\sim 110°$C, [2]. Since during friction both oxymethylene and trioxane are detected, this means that the melting of the polymer surface layers [6] expected at higher temperature of $\sim 169°$C [7] is hardly attained in our experiments. The absence of thermal and triboinduced decomposition products in the steel–POM pair is apparently caused by variations in the conditions of the shear force transfer through the POM transfer layers at steel. This prevents friction force to attain F_{fr} transition detected in the POM–POM pair. The quantity of monomer released during friction in the POM–POM pair estimated via the flow-power balance equation during pumping [2] is $\sim 10^{16}$ pieces for the POM–POM pair ($\sim 0.01\%$ of Δm). Notice that the number of macromolecules with the molecular weight typical of POM ($M_n \sim 5 \cdot 10^4$ g/mol) in the of volume with mass Δm is $\sim N_a \Delta m / M_n \sim 10^{15}–10^{16}$ pieces (N_a is the Avogadro number). A single macromolecule rupture can result in

formation of up to a hundred of monomers [8]. Thus, the proportion of macromolecules broken during friction in the POM–POM pair under the conditions of our experiments may be estimated as a value attaining few percent of the number of macromolecules in the volume of mass Δm.

Fig. 1, b illustrates F_{fr} dependences on friction path length ($l = Vt$) under atmospheric conditions for pairs POM–POM and steel–POM used to prepare samples for PITL experiments ($F_n = 14$ N, $V = 0.021$ m/s). Note that for lower F_n chosen for these experiments the F_{fr} behavior for pairs POM–POM and steel–POM in experiments under atmospheric conditions is still consistent with that described above for friction in vacuum. During friction of the PTFE–PTFE pair (curve 3 in Fig. 1, b), observed is characteristic [9] initial increase in friction force F_{fr} and its gradual decrease to a lower level used in plotting data in Fig. 1, c. Note here, that glass transition temperature (T_g) of PTFE and POM is difficult to measure; theoretically predicted values are ~ 160 and 195 K, respectively [10]. This means that both polymers are in rubber elastic state
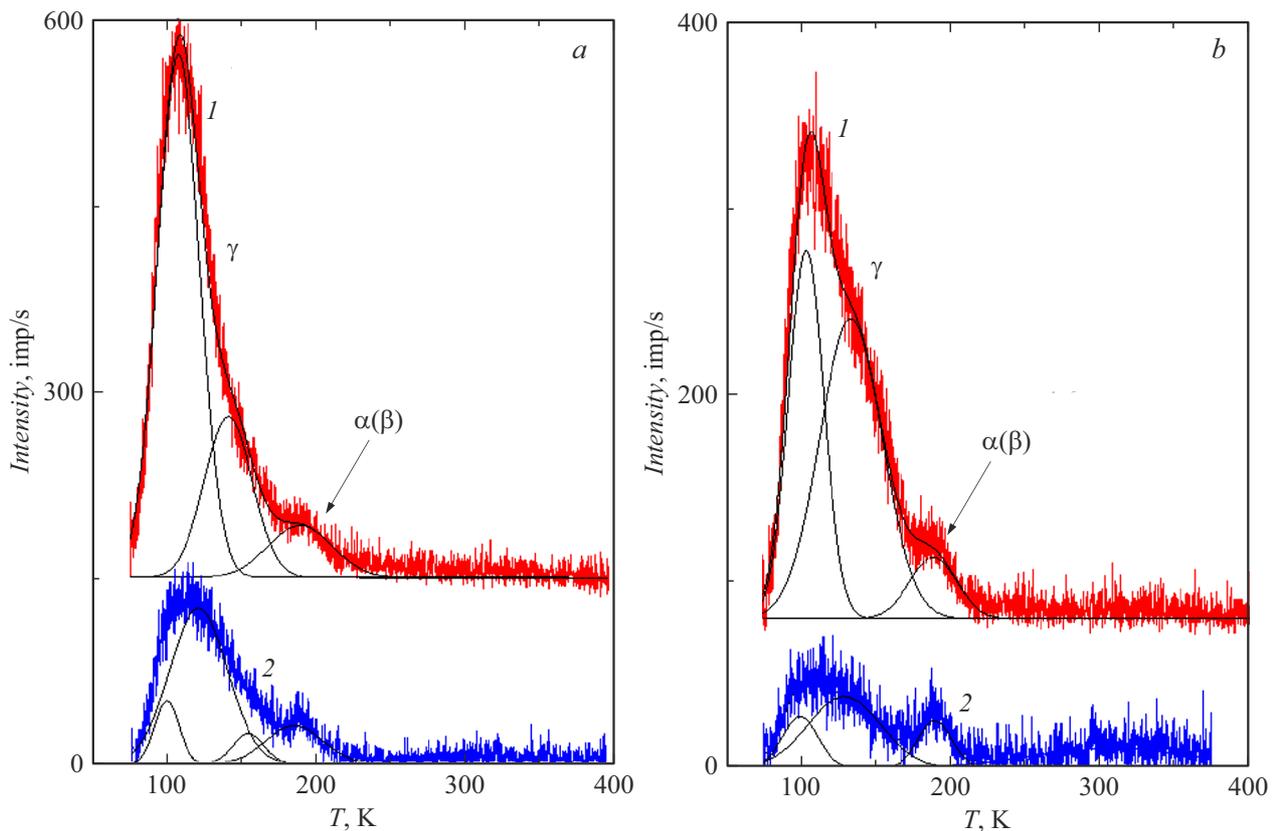
Figure 2. *a* — TL curves for the initial POM film (*1*) and for the same film after friction against the POM cylinder (*2*). The friction conditions are same as for curve *1* in Fig. 1,*b*; *b* — TL curves of the initial POM film (*1*) and the same film after friction against a steel cylinder (*2*). The friction conditions are same as for curve *2* in Fig. 1,*b*. Thin lines illustrate the Gaussian decomposition of the spectra into elementary stages (Fityk 1.3.1 software).

upon friction. Fig. 1,*c* presents typical dependencies of F_{fr} on F_n for pairs POM−POM, steel−POM and PTFE−PPTFE. For the POM−POM pair, the values of coefficient μ in the Amonton−Coulomb law $(F_{fr} = \mu F_n)$ are ~ 0.13 (if calculated from $F_{fr}^{\min}$) and ~ 0.3 (if calculated from $F_{fr}^{\max}$). The values of μ determined from $F_{fr}^{\min}$ are ~ 0.1 for the steel−POM pair and ~ 0.07 for the PTFE−PTFE pair. These values are in good agreement with literature data [6,9]. Notice that the experimental points can be approximated more accurately by functions defined as KF_n^m $(m \leq 1)$ (dashed lines in Fig. 1,*c*). Calculation of the ratio of the friction work $(A = \int_0^L F_{fr} dl$, where L is the total friction path length) to Δm for the POM−POM pair gives $I \sim 18 \pm 5$ MJ/g at the linear sliding speed $V = 0.021$ m/s. In the case of the steel−POM pair, the estimate of I for POM gives slightly higher values, i.e. POM in this pair is more wear-resistant. This correlates with the presence of a sharp F_{fr} transition in the POM−POM pair. These values exceed estimate of I $(\sim 2$ MJ/g) for PTFE measured for of the steel−PTFE pair in [9] at $V \sim 0.2$ m/s. Parameter I is useful, for instance, for estimates of the amount of triboinduced molecular products formed at very low and

not easily measured values of Δm from experimental values of A.

Fig. 2,*a, b* shows PITL curves of POM films subjected to friction against the top of the POM and steel cylinders, respectively. Shapes of the PITL curves indicate the differences in the initial POM surface structure of the samples used in these experiments. The glow curves contain two maxima: at ~ 105 and ~ 190 K. The first one corresponds to γ relaxation (unfreezing of the mobility of individual atomic groups the ends of the macromolecules). Another maximum agrees well with the theoretical estimate of T_g [10] (α relaxation); however, it is possible that this peak contains contribution from β relaxation, i.e. unfreezing of quasi-independent mobility of molecular segments comparable to the Kuhn segment length (in the case of POM reasonable estimate is 5 monomer units [10]). The shift of γ peak towards higher temperatures and decrease of the ratio of its intensity to the intensity of the $\alpha(\beta)$ peak can indicate the erosion of the traps with the energies below 0.08 eV ($T = 115$ K). The similarity between triboinduced variations in the PITL curves for pairs POM−POM and steel−POM can be reasonably explained by the formation of a POM transfer layer on a harder steel surface and

realization of the polymer-polymer friction in this case as well. Stages of the α-, β- and γ-relaxation can be analyzed in more detail by using the curve decomposition (thin lines in Fig. 2). It is reasonable to relate changes in the curve shapes to variations in the conformational composition of short segments consisting of several molecular groups and to dissociation of bonds in macromolecules stretched in the shear field predicted by molecular-dynamics calculations [1].

Thus, in this study a new experimental approach was developed to investigate correlations between the friction parameters, triboinduced rupture of macromolecules, and variations in the molecular dynamics at the interface after friction. The approach will be useful in further studies of the nature of polymer friction in a wider range of friction conditions.

Conflict of interests

The authors declare that they have no conflict of interests.

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