Formation of decomposition products of macromolecules upon friction of polymer against polymer

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The formation of decomposition products of macromolecules was found upon friction of polyoxymethylene against polyoxymethylene in the vacuum of mass-spectrometer . Their composition is shown to be different from that of the products of thermal decomposition of polyoxymethylene. It is shown that the formation of decomposition products is accompanied by the transition of the friction force from low to high level. The effect has been interpreted by the mechanical rupture of macromolecules upon friction. Quantitative parameters of the process have been discussed.

**Keywords:** friction, mass-spectrometry, polymer, vacuum.

Interrelated processes of deformation of subsurface polymer layers, their heating, and bond rupture of macromolecules accompany polymer friction [1,2]. Quantitative examination of these processes is of considerable interest since they may govern the technologically important macroscopic wear of the polymer. In our earlier studies [3,4] it has been demonstrated that mass-spectrometry (MS) provides meaningful data on the formation of macromolecule decomposition products immediately in the process of polymer friction. In the present study, this method is used to examine the correlation between macromolecule decomposition processes and the friction force in the vacuum of mass spectrometer.

A friction test machine operated in the vacuum of an MSKh-6 reflectron time-of-flight MS (Fig. 1, a) was used. Spectra were measured at an energy of ionizing electrons of ~ 100 eV. Friction was examined in the thust bearing geometry (see the inset in the lower left corner of Fig. 1, a). The measurement diagram is presented in Fig. 1, b. Sample *2* is rigidly fixed at the surface of freely rotating table *1*. The table is restrained from rotation by rigid rod *3* at a distance equal to table radius R (13 mm). One end of the rod is fixed at the edge of the table, and the other is secured to strain gauge beam *4*. The signal from the strain gauge beam registered in the Arduino IDE environment [5] is synchronized with the registration of mass-spectrum and pressure in the MS vacuum chamber by using Labview software. A hollow cylinder is pressed against a flat counterbody by normal load F_n (Fig. 1, a) applied via a spring mechanism [5]. With the cylinder rotating about its axis at frequency ν, friction between the flat top of the cylinder and the flat counterbody induces torque $M = F_b R$ of the table, where F_b is the force measured by the strain gauge beam. Integrating relation $M = dF_{fr}r$ in polar coordinates [6] over radius r from r_1 to r_2 and

angle θ (Fig. 1, b), gives the relation for friction force: $F_{fr} = (3/2)F_b R(r_2^2 - r_1^2)/(r_2^3 - r_1^3)$. The values of r_1 and r_2 are measured after the experiment by examining the friction track (Fig. 1, c). They correspond to the inner and outer radii of the hollow cylinder with an accuracy of ~ 0.1 mm. The maximum initial contact pressures are attained at the edges of the cylinder. As they undergo initial higher wear, the distribution of pressure over the contact area becomes more uniform (Fig. 1, c) [7].

Hollow cylinders 18 mm in height with outer and inner diameters of 9 and 6 mm and plates with a thickness of ~ 2 mm and lateral dimensions of $\sim 15 \times 20$ mm were fabricated from commercial polyoxymethylene (POM; POM-H polymer produced by Ticona^{TM} was used), poly(methyl methacrylate) (PMMA), and polytetrafluoroethylene (PTFE). Contact surfaces were polished to roughness $R_a \sim 0.5 \mu$m determined with a Mahr PS10 profilometer. Prior to friction testing, samples were rinsed with warm distilled water and dried for several hours. The melting points of POM and PTFE are 440 and 600 K, respectively [8]. The glass transition temperature of POM is not easy to measure [9]; its theoretically predicted value is ~ 180 K [10]. The glass transition temperature of PMMA is ~ 378 K [8]. Different research groups have reported estimates of the glass transition temperature of PTFE within the range of $\sim 160-400$ K [8]. Friction was initiated at room temperature of samples ($\sim 22°$C) in the static friction mode. Prior to experiments, counterbodies were held under load in vacuum for 1 h. Experiments were initiated at a residual pressure of $\sim 10^{-6}$ Torr in the MS.

Figure 2, a presents the typical temporal dependences of the friction force at a constant sliding speed for a POM$-$POM pair and two F_n values. Force F_{fr} undergoes a transition from the lower level to the upper one (curves *1, 2*) in the course of friction tests. The value of μ in the
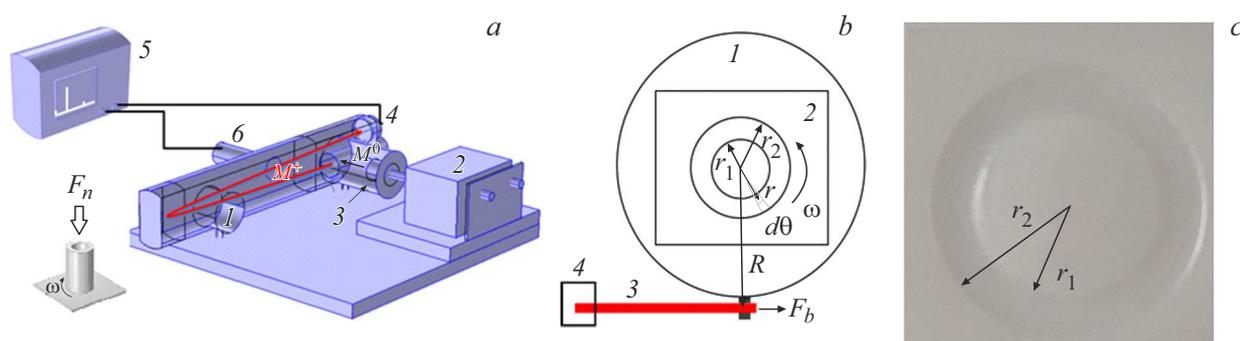
Figure 1. *a* — Overall view of a mass spectrometer with a friction test machine connected to its flange. *1* — To an Adixen turbomolecular pump, *2* — geared motor, *3* — friction machine (see panel *b*), *4* — ion detector, *5* — DPO3032 Tektronics digital oscilloscope, and *6* — Dual Mag 972B pressure gauge. The red line in the ion drift tube (a color version of the figure is provided in the online version of the paper) denotes the trajectory of M^+ ions formed upon ionization of neutral M^0 molecules produced in the process of friction. *b* — Geometry of measurement of the friction force (see text): holder table *1* for sample *2* and rigid rod *3* fixed at the strain gauge beam *4* and the edge of the table. $d\theta$ — angle element of the elementary friction area and ω — rotation direction. *c* — Typical shape of the friction track on the surface of POM.
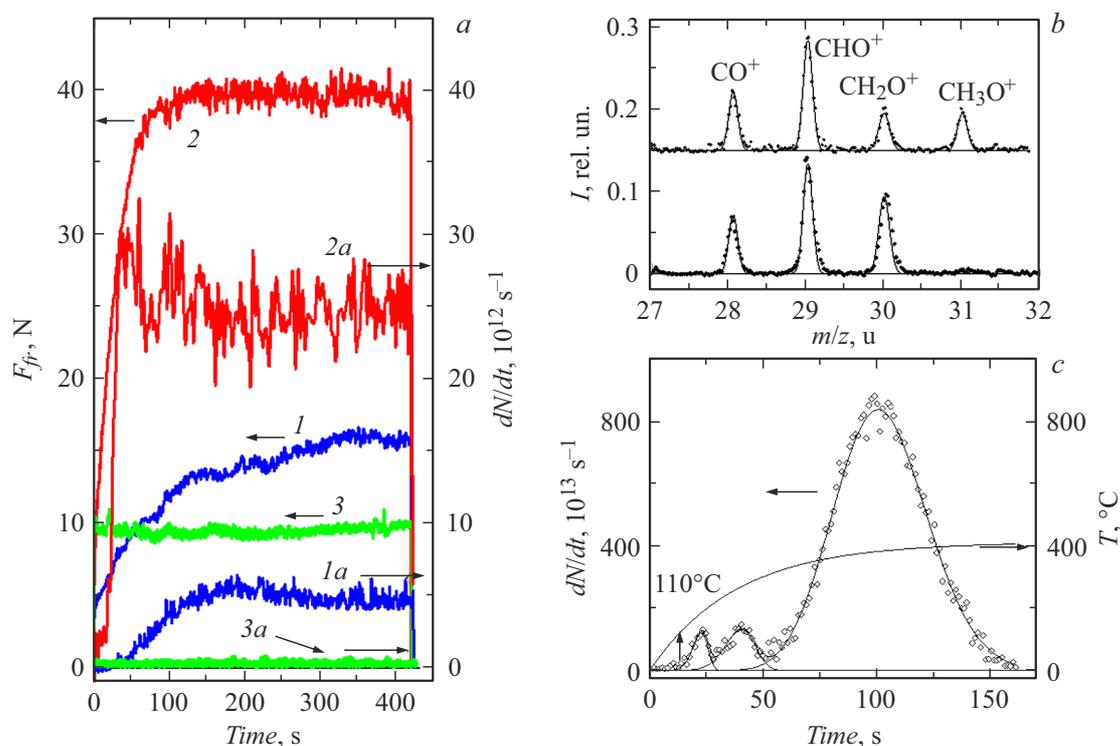
Figure 2. *a* — Dependences of the friction force (*1*−*3*) and the rate of formation of tribodestruction products (*1a*−*3a*) versus time (calculated with respect to oxymethylene) for POM−POM (*1, 1a, 2, 2a*) and PMMA−POM (*3, 3a*) pairs. Normal loads of ~ 40 (*1, 1a*) and 100 N (*2, 2a, 3, 3a*) were applied. The mean linear sliding speed $\sim 0.021\,\mathrm{m \cdot s^{-1}}$. *b* — Mass spectra of tribodestruction products (upper spectrum) and thermal decomposition products (lower spectrum). *c* — Thermal decomposition spectrum of a thin POM layer (the layer was produced by rubbing POM onto tantalum foil-heater) registered as the intensity of oxymethylene in in the course of heating with an exponentially decreasing rate, $T[°\mathrm{C}](t) = 411 - 403e^{-t/38[s]}$.

Amontons−Coulomb law ($F_{fr} = \mu F_n$) is ~ 0.12 for the lower level and ~ 0.4 for the upper level. In the mass-spectrum the growth of friction force is accompanied (the upper spectrum in Fig. 2,*b*) by an increase in intensity of oxymethylene (H$_2$CO, characteristic peaks with $m/z = 29$, 30, 28 u) and trioxane (C$_3$H$_6$O$_3$, $m/z = 31$, 61, 89, 29 u)

lines. The intensities of spectral lines determined by substraction the background spectrum from the spectrum measured in the course of friction or heating are shown in the figure. The growth of intensity of these lines (curves *1a, 2a* in Fig. 2,*a*) saturates when the friction force also reaches saturation. The peak with $m/z = 31$ u

is the most intense in the spectrum of trioxane. It is almost absent in the oxymethylene spectrum. The ratio of intensities of lines with $m/z = 29$ u and $m/z = 31$ u under friction is ~ 3. Neither the transition of the friction force nor the oxymethylene, trioxane, PMMA and PTFE monomer spectrum peaks were detected in similar experiments with, e.g., PMMA−POM, PMMA−PMMA, and PTFE−PTFE pairs at the same sensitivity of MS registration channel (μ for these pairs is $\sim 0.05−0.14$). The behavior of the friction force (curve *3*) and the intensity of monomer lines (curve *3a*) is illustrated in Fig. 2, *a* using the example of a PMMA−POM pair at the maximum F_n used in experiments. POM is in rubber elastic state upon friction tests, while PMMA is in the glassy state. The detected formation of decomposition products induced by the transition of the friction force in a POM−POM pair and the lack of such products in e.g., PMMA−POM pair indicate that the molecular mobility of macromolecules in amorphous POM regions may be of importance in this process. The lower spectrum in Fig. 2, *b* corresponds to a purely thermal impact on POM. The spectrum was obtained upon heating a thin POM film formed by rubbing a POM sample against the surface of tantalum foil-heater. It is evident that the intensity of the line with $m/z = 31$ u is at the noise level in the spectrum of thermal decomposition products of POM. This implies that the mechanism of bond dissociation in macromolecules in the process of friction differs from the mechanism of pure thermal decomposition. Figure 2, *c* shows thermal decomposition spectra of POM monomer (recorded by measuring the intensity of peaks with $m/z = 29, 30, 28$ u) in the process of gradual heating of a POM film (the experimental procedure see elsewhere [11]). The onset of thermal decomposition of POM (i.e., onset of the lowest-temperature stage of decomposition with the release of $\sim 2\%$ of the total amount of monomer produced upon heating) corresponds to a temperature of $\sim 110°$C. Note that the possibility that this stage is a consequence of friction cannot be ruled out yet, since the film was formed in a friction process (see above). The examination of thermal decomposition of the initial POM is made difficult by the need to prepare a film from a solution, since this requires heating the solution [8] and may into polymer destruction.

The measurement of temperature directly in the friction zone is a complicated task, but this temperature can be estimated. In the case of complete conversion of the friction energy to heat, this estimate is the solution of a diffusion problem for two contacting semi-infinite bodies [12]: $\Delta T = (2J/\lambda)(kt/\pi)^{1/2}$ (t is time, λ is the thermal conductivity, $k = \lambda/(\rho C_v)$ is the heat diffusion coefficient, ρ is the density, and C_v is the heat capacity) with a heat source at the interface with specific power $J = F_{fr}V/S$ (V is the linear sliding speed and S is the contact area). If S is equal to the actual contact area (A_0), mean power $J = 2\pi v M/S$ is obtained via integration in our geometry on account of $V = 2\pi r v$. With an even distribution of flows into two identical counterbodies taken

into account, calculations yield $\Delta T \sim 100°$C for curve *1* (Fig. 2, *a*) and $\sim 160°$C for curve *2* at the moment when F_{fr} reaches saturation level. The calculated ΔT value decreases if the removal of heat via radiation and convection is accounted for. POM tribodecomposition products start forming at the very onset of friction (see Figs. 2, *a* and *c*) at calculated $\Delta T \sim 10°$C, which is significantly lower than the onset of the low-temperature thermal decomposition stage (Fig. 2, *c*). Coupled with the identified change in the composition of destruction products under friction (Fig. 2, *b*) compared to those formed upon heating and the lack of detected decomposition products in a PMMA–POM pair, this indicates the mechanically activated macromolecule rupture in the process of friction. The model predicts that the temperature in the friction zone increases in proportion to $t^{1/2}$. This does not agree with the fact that the rate of formation of decomposition products reaches saturation (Fig. 2, *a*). One may note in this context that, e.g., the formation of wear particles alters the conditions of a contact thermal problem. In a more realistic case of a plastic contact between the asperities of rough surfaces, $A_0/S \approx \sigma_n/\sigma_0$ (yield point σ_0 for POM is ~ 140 MPa, $\sigma_n = F_n/S$) [13]. The value of σ_n in our experiments reaches ~ 4 MPa; i.e., A_0 falls within the range from a fraction of a percent to several percents of the nominal area of contact. The time of friction between asperities with size $D \sim 1 \mu$m is $D/V \sim 10^{-4}$ s. Using the estimate of $J = 0.5\mu\sigma_0 V$, one finds a calculated ΔT of several degrees for a single friction contact between asperities. The complete analysis of the of roughness temperature variation is a separate problem.

The monomer amount released in the process of friction in a POM−POM pair can be estimated using the equation of flow's power rate balance upon pumping [14]: $k_B T dN(t)/dt = s\Delta p(t) + V_p d\Delta p/dt$, where Δp is the pressure rise, $N(t)$ is the time dependence of the overall number of desorbing molecules, k_B is the Boltzmann constant, T is temperature, V_p is the volume of the vaccum chamber, and s is the pumping rate ($s = 0.1$ m$^3 \cdot$ s^{-1}, $V_p \sim 0.02$ m^3). The curves in Figs. 2, *a*, *c* were plotted by using this recalculation. The amount of depolymerization products per a single bond rupture in the process of thermal decomposition of POM may reach several hundred monomers [15,16]. With this estimate taken into account, the friction energy flow needed to reach the detected rupture intensity for bonds with a bond energy of ~ 300 kJ/mol is approximately seven orders of magnitude lower than the friction power (the latter is $\sim 0.1−1$ J/s). An MS estimate obtained for mechanical dispersion of PMMA was approximately four orders of magnitude higher [16]. Calculations reveal that the number of molecules produced in our experiments is $\sim 10^{16}$. This amount corresponds to the thickness of decomposed POM layers of several nanometers.

The possibility of bond dissociation in macromolecules upon their orientation under friction was predicted, e.g., in molecular dynamics calculations [2]. An increased force of friction between the surfaces of polystyrene

and poly(vinylbenzyl chloride) with bond-broken macromolecules formed by ultraviolet radiation was detected in experiments reported in [17]. In the case of a POM−POM pair, decomposition occurs directly in the process of friction. It is reasonable to assume that the segmental mobility of POM macromolecules in a POM−POM pair (i.e., in a homogeneous friction pair of polymers at a temperature above the glass transition [9,10]) induces interpenetration of macromolecules of counterbodies. The stretching of these macromolecules in a shear field at the interface can increase the friction force, can result in bond ruptures in a macromolecule, and in a chain reaction of macromolecule decomposition within subsurface layers. This process may be the source of defects that induce the formation of macroscopic wear particles.

Thus, it was demonstrated that for a homogeneous POM−POM friction pair (polymer which exists in rubber elastic state in friction conditions) the friction force undergoes a transition from low to high level. This transition is in straightforward correlation with the formation of tribodecomposition products of POM macromolecules. The formation of decomposition products has been attributed to an increase in segmental mobility of macromolecules, which can result in interpenetration of POM macromolecules (and their subsequent rupture at the interface in the course of chain stretching occurring upon shear of counterbodies) and induces an increase in friction force. The obtained results may help in clarifying the nature and in obtaining quantitative estimates of macroscopic wear of POM−POM [18] and other friction pairs. This may require investigation of polymer pairs in a wider range of friction parameters.

Conflict of interest

The author declares that he has no conflict of interest.

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Translated by D.Safin