THE ION EMISSION DURING THE FRACTURE OF POLYMERS

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The results of the study of charged particle emission in the course of the rupture of polymer film samples in the high vacuum have been presented. Regularities of ion emission at the last stages of the stretching are associated with peculiarities of the main crack's intergrowing. Calculations of ion-motion trajectories within the crack were carried out. It was established that the ions emitted from the crack tip on the sample surface were recorded experimentally while the crack growing. The emitting region size and the emission current level were estimated. Mechanisms of formation of low-molecular ions during polymer fracture were discussed.

Key words: emission, ion, mechanoemission, ionization of macromolecules, crack

Introduction

Experimental and theoretical study of the processes occurring during the propagation of a main crack in polymers has long attracted the attention of researchers [1 − 7]. The thermophysical properties of a growing crack are discussed in [1 − 3]. Ref. [1] presented a physical model of a polymer heated near the crack tip and described experiments whose results were in good agreement with theoretical predictions. The change in temperature with time in polymethylmethacrylate is due to sequential stretching and breaking of polymer chains in micro-regions about 130 μm in size, located along the trajectory of crack propagation [2]. The effect of heat released under viscoplastic shear on polymer strength was considered in [3]. Refs. [4, 5] were dedicated to the propagation rate of the main crack; Ref. [4] established the role of strain hardening in the process of macroscopic crack propagation in polyolefins. Non-uniform motion of a crack in a polymethyl methacrylate plate was observed experimentally using an ultrafast streak camera both for quasi-static and impulse loading [5]. The fracture regions at the crack tip of glassy polymers were investigated by optical interferometry [6]; it was revealed that the size of these regions can reach tens of microns. The nature of polymer strength remains an important issue, and new methods should be used to study the processes occurring during polymer fracture (in particular, at the molecular level).

Deformation and fracture of polymers in vacuum are accompanied by emission (mechanoemission) of charged particles (electrons and ions). Emission of electrons during the deformation of polymers has been studied in sufficient detail [7 − 9]; considerably less attention has been paid to mechanoemission of ions. Emission of charged particles was investigated in [9 − 13] both in the pre-fracture stages of sample loading and under fracture. The studies in [9] were mostly limited to filled polymers where fracture occurs at the interface and leads to long-lasting post-emission of positive ions after sample failure. Emission of positive ions during the deformation of polyethylene at the pre-fracture stage was detected in the experiments described in [10, 11]. Ref. [12] reported on the emission of both positive and negative ions during the propagation of a main crack in a number of polymer films. The emission of positive ions was also detected under fracture of auto-adhesive compounds of amorphous polymers formed at temperatures below the bulk glass-transition temperature [13].

It was revealed in [8, 14, 15] for mechanically stressed polymers that a transition of electrons to deep traps may occur with subsequent decay of weak interatomic bonds in the generated positive macroions due to a decrease in the ionization energy of elongated macromolecules. The observed mechanoemission of

cations is likely associated with this separation of charges and with the rupture of interatomic chemical bonds in the macromolecules under stress. It is assumed in [12] that anions form because electrons in polymers can be captured by atomic groups with a positive electron affinity. Ref. [16], reporting on polypropylene fracture in a ball mill at 77 K, found using the EPR method that the electrons were captured by the molecules of the acceptor (tetracyanoethylene), specially embedded into the bulk of the polymer. This indicates that some of the electrons attach to neutral molecules, with negative ions forming, in the regions where fracture occurs.

Apparently, positive ions are emitted in the form of low molecular weight fragments of molecules. It was discovered in [17], where a loaded atomic chain was studied by the molecular dynamics method and the Morse potential was used to describe the interatomic interaction, that a stretched chain of atoms breaks into several fragments upon release, as a result of propagation of a relaxation wave. The chain consisted of forty atoms and was stretched with a force equal to 0.99, corresponding to the tensile strength of the interatomic bond. The first fracture of the chain was associated with superposition of tensile pulses (the incident and the reflected from the fixed end). Fracture of the fragments that broke away occurred due to reflection of waves from the free ends formed and their interference.

A polymer near a growing crack heats up to a temperature $T = 500$ K [18, 19], and up to $T > 1000$ K according to the data of [20, 21]. Thermal degradation of polyethylene terephthalate occurs at a sufficiently high rate at a temperature $T \approx 560$ K [22]. The emission of ions might be caused by thermal desorption of low molecular weight fragments of molecules from the polymer surface.

This study is dedicated to measuring the intensity of ion emission that occurs under fracture of polymer films of different thicknesses in vacuum; the trajectories of ions have been calculated. Our goal has been to determine whether the emission of ions from a crack can be detected, and to assess the sizes of the emitting region and the level of the emission current.

Experimental procedure

The experimental samples were industrial films of polyethylene terephthalate (PET) and PM-1 polyimide (PI). The dumbbell-shaped samples were mounted in a vacuum chamber using metal clamps and insulating sleeves. The widths of the working part of the samples were 1.0; 1.8 and 8 mm, and their length was 5 mm. The thicknesses of the samples were 20 and 100 μm for the PET films, and 40 μm for PI. The samples were deformed at room temperature at a constant rate of 25 mm/s (the samples were not notched). The samples were stretched in a stainless steel chamber at a residual gas pressure no more than 10^{-7} mm Hg and at room temperature.

The emission intensity was measured in the particle-counting mode using a VEU-6 secondary electron multiplier with a grounded cathode. The multiplier was located at a distance $L = 0.28$ m from the sample so that a magnetic field could be generated between the sample and the particle detector. As we measured mechanoemission, a transverse magnetic field was induced with two flat permanent magnets in order to separate the ionic component in the current of negatively charged particles through deflecting the electrons by this field.

The magnetic induction in the central region between the magnets was 0.036 T.

To separate the emission current, the particles were accelerated in the gap between the insulated electrode and the grounded grid installed at the input of the drift space (flight tube). For this purpose, a potential of 1000 V, whose sign coincided with the sign of the charge of the detected particles, was applied to the electrode. The distance between the electrode and the grid was $l = 22$ mm (Fig. 1,b). Since the setup had only one detection channel, particles with the charge of only one sign could be detected in testing one sample. The pulses from the particle detector were amplified and simultaneously fed to an intensity meter with a resolution of 1 ms and a time analyzer with a resolution of 1 μs. The intensity meter and the time analyzer, the tools for tuning and adjusting them, and the means for visualizing the time dependences, including the sample loading curves were implemented via a personal computer with the corresponding

software. The experimental setup and the emission detection system are described in more detail in [12]. To assess the actual duration and nature of the emission under sample fracture, the signal was simultaneously fed to the time analyzer with a resolution of 1 μs, triggered by pulses corresponding to the intergrowth of the main crack.

Experimental samples and discussion

A typical dependence of the emission of negative particles on time t under deformation

a)

b)

Fig. 2. Loading kinetics F for a polyimide film sample (lines with arrows) and the dynamics of the emission of negative particles from the sample under stretching (the vertical segments are the number of pulses J_m recorded per 1 ms), without (*a*) and with (*b*) a magnetic field applied. The thickness of the sample was 40 μm, the width was 1.8 mm. The tensile speed was 25 mm/s
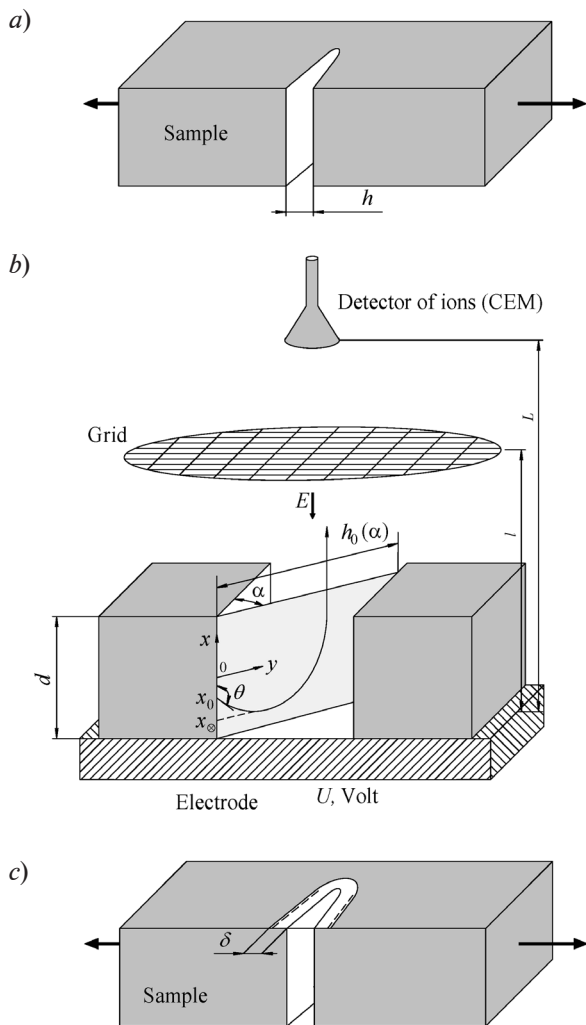
a)

b)

c)

Fig. 1. Schematics illustrating sample fracture and ion emission from a crack in the polymer: *a* is a stretched sample with the main crack; *b* is the layout of the experimental setup and the parameters of the ion trajectory; *c* is the emitting region of width δ on the surface of the film
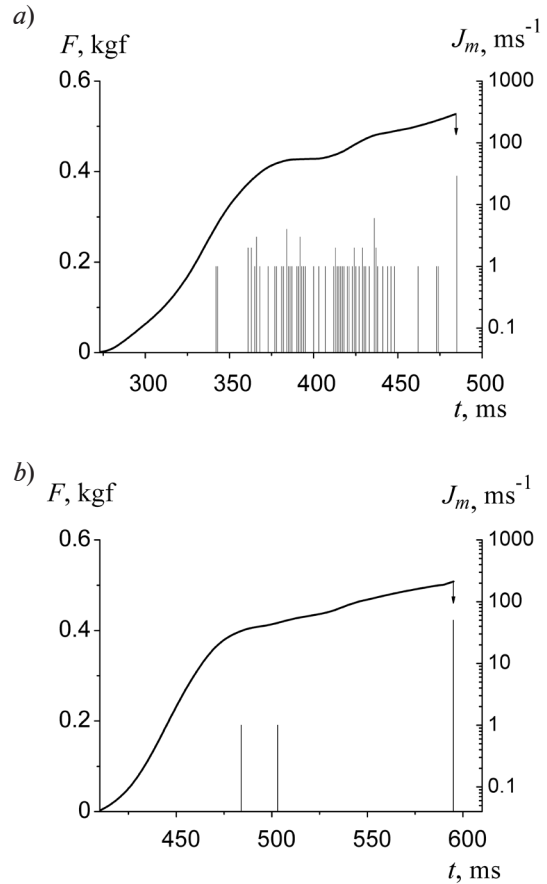
of a PI film is shown in Fig. 2. This emission was detected by the number of pulses J_m generated per 1 ms.

Arrows indicate rupture times. Similar $J_m(t)$ dependences were observed for other polymers. Evidently, only individual negative ions are emitted in the presence of a magnetic field until the film ruptures (electrons do not enter the multiplier). The number of negatively charged particles emitted at the time of rupture practically does not depend on the absence or presence of the magnetic field. This means that negative ions are emitted during crack propagation, and the electron emission component is absent.

The dependences similar to those shown in Fig. 2,*b* were also recorded for positive ions. In this case, a positive potential was applied to the electrode, and the corresponding retarding electric field stopped the negative particles. Thus, both positive and negative ions are emitted during polymer rupture. It can be seen from Fig. 2 that the emission burst at the instant of rupture lasts no longer than 1 ms.

The results of determining the actual duration and nature of the emission under sample rupture for PET films of different thicknesses, conducted simultaneously with the above-described experiments (see Fig. 2), are presented in Fig. 3 as the dependence of the emission intensity J_μ of negative ions on time. Apparently, the samples whose thicknesses differed by a factor of five had the same emission intensity. Only the duration of the emission and, accordingly, the total number of detected ions differed, since the samples had different widths. The duration of the emission increased with increasing sample width. For example, emission lasted three times longer for the samples with a width of 8 mm than for the samples with a width of 1 mm. Pauses in emission, whose number increases for wider samples, are also clearly visible. As established in [12], a sharp decrease in ion emission intensity is associated with the retardation of the main crack. The times of occurrence and the duration of the pauses in emission depend on the physico-mechanical properties of the polymer.

These results confirm the conclusion made earlier in [12], where it was found that the observed ion emission occurs only when the crack moves. That study also proposed a method for calculating the emission current taking into account the cross-sectional area of the sample. The emission intensity determined using this method was in good agreement with the experimental results.

Let us now discuss the absence of the dependence of ion emission intensity on film thickness that we have observed (see Fig. 3).

Calculation of the coefficient of ion emission from the crack

The coefficient of ion emission from the crack has to be determined to calculate the ion emission current. It follows from our experi-

ments that ion emission follows the motion of the crack without inertia. This is confirmed, in particular, by the fact that the pauses in emission intensity shown in Fig. 3 start and end quickly. Emission is observed in the first microseconds after fracture evolves in the sample (the start of the intergrowth of the main crack). The crack opens to $h = V_d t_0 = 0.025$ μm in time $t_0 = 1$ μs at a tensile speed $V_d = 25$ mm/s. Since approximately the same number of ions is emit-
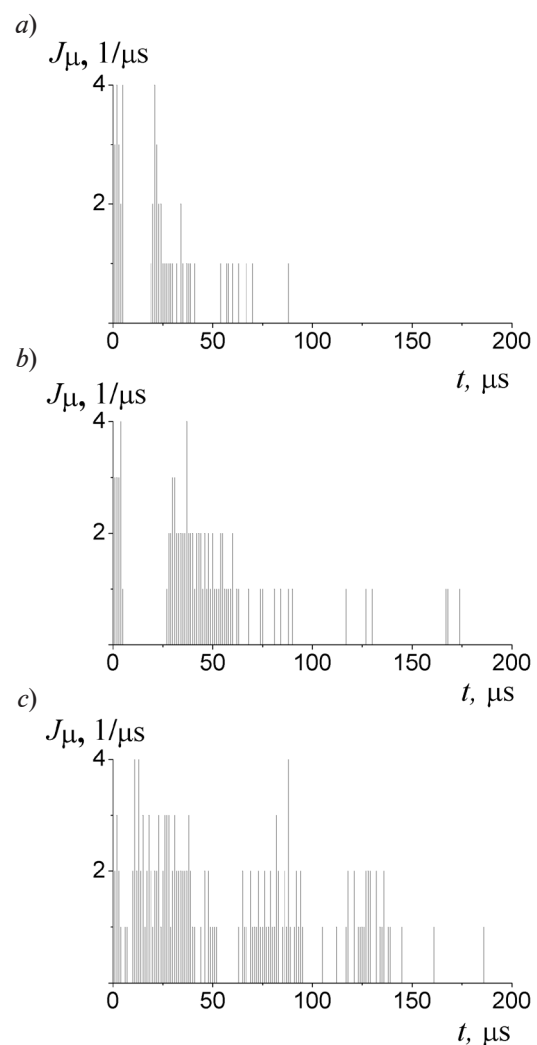

Fig. 3. Dynamics of emission intensity of negative ions (J_μ is the number of pulses recorded per 1 μs) during crack propagation in PET samples with different thicknesses d and widths B: $a - d = 100$ μm, $B = 1.0$ mm; $b - d = 20$ μm, $B = 1.8$ mm; $c - d = 20$ μm, $B = 8$ mm.
The tensile speed for the film stretching was 25 mm/s

ted each microsecond during the intergrowth of the crack, we assume that the distance between the walls of the crack near its tip is $h = 0.025$ μm. The crack propagation velocity in PET was found in [12] to be $V_c = 40$ m/s (the duration of ion emission was used in the calculations). Thus, the crack should move by 40 μm each microsecond, (see Fig. 1, *a*, *b*).

In order to determine whether the ions that have escaped from the walls of the crack are detected, we calculated all possible trajectories of the ions emitted from different points of the crack wall at different angles. Since the trajectory of an emitted ion lies in a plane passing through the vectors of initial velocity and electric field strength, the three-dimensional problem can be reduced to a two-dimensional one by searching through the ion trajectories lying in these planes. For this purpose, we solved the equation of motion of an ion in a plane parallel to the vector **E** and making an angle α with the wall of the crack. As a result, we obtained an equation for the particle trajectory in rectangular coordinates *x*, *y* with the origin at ($d/2$, 0) (see Fig. 1,*b*):

$$x(y) = x_0 + y \ \text{ctg}\theta + \frac{y^2}{4\sin^2\theta}\frac{qE}{W}, \quad (1)$$

where x_0 is the initial exit coordinate, θ is the angle between the vector of the initial particle velocity and the *x* axis, *q* is the unit charge, $E = U/l$ is the retarding electric field strength (*U* is the electrode potential, *l* is the distance between the electrode and the grid), $W = kT$ is the initial particle energy (*k* is the Boltzmann constant).

Next, we determined the number N_e of particles that escaped from the crack. Let us denote the total number of the emitted particles as N_s, which is expressed as

$$N_s = n_x n_\theta n_\alpha, \quad (2)$$

where the numbers *n* are equal to the number of points taken for calculation by the corresponding coordinates. The variation ranges of the numbers *n* with respect to the coordinates x_0 and θ are obvious.

The greatest value of the angle α is determined by the crack propagation velocity V_c:

$$\text{tg}\alpha_m = \frac{2h}{V_c t_0} = \frac{2V_d}{V_c}. \quad (3)$$

We assumed that only those ions whose trajectories did not intersect the opposite wall of the crack and the surface of the electrode escaped from the crack. Therefore, the first condition for determining the number of ions escaped from the crack is the following: $x(h_0) > d/2$. The second is the condition for the turning point: $x_\otimes > -d/2$. With these conditions in mind, the following formula holds true for the relative number of emitted ions:

$$\eta_e(\alpha, \theta) = \frac{1}{N_s}\sum_1^{n_x}\Phi\left\{\left[x[h_0(\alpha)] - \frac{d}{2}\right]\right\} \times$$
$$\times \Phi\left[x_\otimes(\theta) + \frac{d}{2}\right], \quad (4)$$

where Φ is the unit step function, and

$$x_\otimes(\theta) = x_0 - \frac{dW}{Uq}\cos\theta, \quad (5)$$

$$h_0\alpha = \frac{V_d \cdot t_0}{\sin\alpha}. \quad (6)$$

Then the coefficient of ion emission from the crack can be defined as

$$\eta = \frac{1}{N_s}\sum_1^{n_\alpha}\sum_1^{n_\theta}\eta_e(\alpha, \theta). \quad (7)$$

The results of calculating the values for $n_x = n_\theta = n_\alpha = 800$ are given in Fig. 4, which shows the angular dependences of the ion emission coefficient. It can be seen that mainly the ions escaping at an acute angle to the surface of the wall can escape the crack. The initial energy of the ions has a noticeable effect on $\eta_e(\alpha, \theta)$, while the retarding field is weak. The potential $U = 1000$ V, for which η_e is about 10^{-5}, is typically used in the experiments. Ion emission at grazing angles is energetically unfavorable because ions are attracted by their own images. Apparently, however, ions also cannot be extracted frin the crack at angles approaching $\pi/2$ even with a thermal initial velocity. In addition, since the charges formed on the walls of the crack are distributed unevenly, electric fields directed perpendicular to the walls can be generated between them, preventing charged particles from escaping the crack (regardless of the direction of these fields). If the field accelerates the ion, then it most likely falls on

the opposite wall. The retarding field generates an additional potential barrier that prevents ion emission from the surface of the crack wall.

Even though we chose favorable conditions for ion emission from the crack, the calculated value of the emission coefficient turned out to be very small: $\eta \approx 0.01$:

To correctly estimate the intensity of ion emission from the crack, we need to multiply the intensity value calculated in [12] (equal to 10 ions/μs) by the value of η. Thus, we can conclude that it is practically impossible to capture ions from the crack by a detector located at a distance $L = 0.28$ m from the sample. Consequently, we mostly detected the particles that escaped from the surface of the sample through the tip of the crack during polymer rupture.
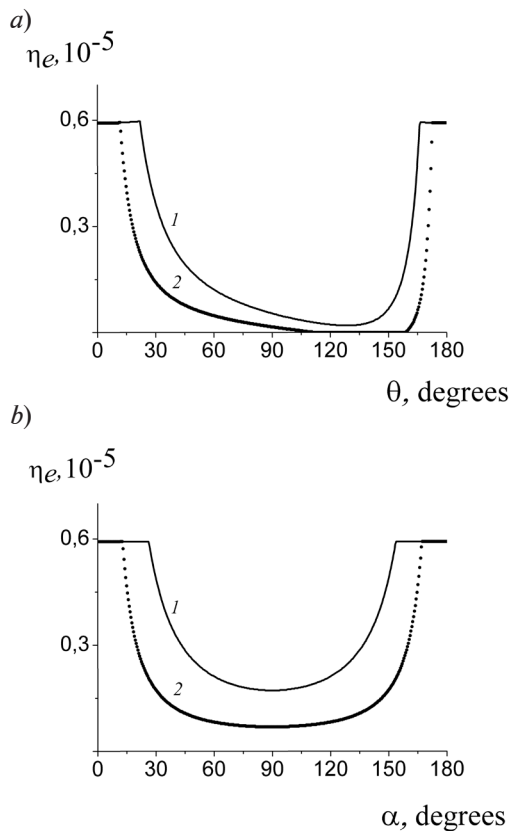
a)

$\eta_e, 10^{-5}$

b)

$\eta_e, 10^{-5}$

Fig. 4. Calculated angular dependences of the coefficients $\eta_e(\theta)$ (*a*) and $\eta_e(\alpha)$ (*b*) of ion emission from the crack with fixed values of the second angle: $\alpha = 0.52^{\cdot}$ (*1*), $0.97^{\cdot}$ (*2*) (*a*) и $\theta = 0.52^{\cdot}$ (*1*), $0.97^{\cdot}$ (*2*) (*b*). The electrode potential $U = 1$ kV, the initial ion energy $W = kT$, $T = 580$ K

Calculation of the intensity of ion emission and estimation of the size of the emitting region

Since intense processes of macromolecular rupture and heat generation generally occur near the crack tip, we can assume that ion emission also takes place in this region. The region where intense rupture, deformation, and heating evolve during crack propagation is known to be several tens of microns thick [6].

Let us assess whether our data are in agreement with these concepts. Let us denote the width of the emitting region of the polymer adjacent to the edge of the crack (see Fig. 1,*c*) as δ. Suppose that each rupture of a macromolecule produces one fragment (ion) with a low molecular weight. If we regard ion emission as the thermal desorption of low molecular weight fragments from the surface of the polymer, then the following equation holds true for the emission intensity J [23]:

$$J = \nu \cdot N_0 \cdot \exp\left(-\frac{\varphi}{kT}\right), \qquad (8)$$

where ν is the frequency factor, N_0 is the number of ions produced, φ is the activation energy (ion detachment energy).

Let us assume that ions only escape from a layer with the width approximately equal to the diameter of the macromolecule ($\phi = 1$nm) from the surface facing the detector. To estimate the value of N_0, we assume that the emission occurs from the polymer volume ΔV formed during the time Δt as the crack moves with the velocity V_c:

$$\Delta V = 2V_c\Delta t\phi\delta.$$

To detach from the polymer surface, the ion has to acquire an energy exceeding the energy of the interaction between the charge and the induced dipoles. The energy it takes to remove a unit charge q from the dielectric surface is expressed as follows [24]:

$$\varphi \approx \frac{\varepsilon - 1}{16\pi\varepsilon_0(\varepsilon + 1)} \frac{q^2}{\hat{y}}, \qquad (9)$$

where ε is the relative permittivity of the dielectric, ε_0 is the electric constant, and $\hat{y}$ is the average distance between the electric charge and the surface.

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In case of isotropic emission, the fraction of particles K entering the detector is equal to the ratio of the area S_d of the detector's entrance window to the area of a sphere with the radius L:

$$K = \frac{S_d}{4\pi L^2}. \quad (10)$$

The estimate of the concentration of macromolecular ruptures made in [25] for oriented (by 5.5 times) polymers yielded the value $n \approx 10^{25}$ m^{-3}. In our experiments, non-oriented samples ruptured at an approximately double elongation. In addition, a plastic deformation developed at the tip of the crack, reaching 60% in PET [26]. Therefore, we can assume that the concentration of macromolecular ruptures was of the same order for the rupture of our experimental polymer samples. Then the quantity $N_0 = n\Delta V$ and only $N_0 K$ ions fall into the detector. Equating this value to the detected N_μ value (the number of ions emitted per 1 μs), we obtain for δ the expression

$$\delta = \frac{N_\mu}{2n\nu\Delta t V_c l_0 K} \cdot \exp\left(\frac{\varphi}{kT}\right). \quad (11)$$

It follows from the data in Figs. 2 and 3 that the detected ion emission intensity is $1 - 4$ μs^{-1}. Therefore, for $Dt = 1$ μs, $\hat{y} \approx 0.1$ nm, $\varepsilon = 3$, $\nu = 10^{13}$ s^{-1} and for the temperature $T = 580$ K (the onset of thermal degradation in PET [22]), we obtain value $d \approx 20$ μm. From this we can conclude that the area of the fractured material near the surface of the rupture extends to tens of microns around the crack. Consequently, as the main crack propagates, a narrow fracture region adjacent to the crack's edges forms on the surface of the sample.

Results and discussion

Comparing Figs. 2, *a* and *b*, we can see that electrons make the main contribution to the current of negatively charged particles at the pre-rupture stage of polymer deformation. The ionic component becomes dominant in the current of negatively charged particles at the instant of rupture (when the main crack is propagating), i.e., when the fracture process is localized, as evidenced by the weak effect of the magnetic field on the emission intensity at the

time of sample rupture. It was noted above that charges in the polymer are formed by oppositely charged pairs, so the number of positive ions is equal to the number of electrons. Not all ions and electrons are emitted from the surface of the heated polymer. The emission intensities of positive and negative ions are the same. Electrons that could be emitted are not detected during crack intergrowth. Therefore, if the fracture is localized, the probability of electron capture by neutral macromolecular fragments increases practically to unity, apparently due to an increase in the concentration of decay products of strained polymer chains. The lifetimes for autodetachment states of negative ions of complex molecules formed as a result of electron attachment to the corresponding molecules depend on the number of vibrational degrees of freedom for these molecules and amount to tens of microseconds [27]. Therefore, a considerable fraction of the negative ions emitted during propagation of the crack reaches the particle detector. Electrons can get captured by molecules both in the condensed and in the gas phase. The attachment of electrons to molecules in the condensed phase is facilitated by an increased number of possible energy transfer channels generated by molecular interactions. Therefore, the cross-section of electron attachment to molecules is much larger in the condensed phase than in the case of free molecules. In addition, the transition from autodetachment to stable states is facilitated, since the excess energy during the transition of the ion from the autodetachment to the stable state is expended on excitation of the molecule's vibrational degrees of freedom. It is also known that the cross-section of electron attachment to a vibrationally excited molecule is much larger than for a molecule in the ground state. This means that the increase in temperature during polymer fracture and the associated vibrational excitation of the molecules lead to an increase in the cross-section and in the electron attachment rate constant. Importantly, energy redistribution can facilitate the desorption of negative ions in the process of electron attachment to the surface molecules of the polymer [27].

The processes of electron attachment to atomic systems are resonant and occur in the

electron energy range from tens of meV to eV. In our experimental conditions, with the voltage $U = 1000$ V and a 22-mm distance between the grid and the electrode (see Fig. 1,b), the electrons manage to acquire the necessary energy near the surface of the polymer, where the emission of volatile products is the highest [28]. For this reason, electrons can also attach to molecules in the gas phase. In this case, due to a decreased number of possible energy transfer channels, the ion may have no time to self-stabilize and decay. As a rule, however, complex electronegative molecules have stable negative ions.

The fractured polymer acting as a new ion source can provide the opportunities for studies of negative ions that are unavailable with traditional ion sources used in negative ion mass spectrometry, limited by the vapor pressure of the test substance [29].

Conclusion

We have carried out experimental and theoretical studies on polymer rupture, establishing that the emitting regions near the tip of the main crack act as the ion sources. These regions have a width of about 20 μm and a length depending on the propagation velocity of the crack. The ion emission from the depth of the crack is less than 1%, and the cross-sectional area of the sample has little effect on the emission intensity as a result. The kinetics of ion emission under rupture of a polymer sample is governed by the process of macrocrack propagation, which is determined by the properties of a specific polymer.

The method of mechanoemission of ions proves to be extremely effective and makes it possible to obtain new data on the characteristics of the processes that occur during polymer fracture.

Measuring the current-voltage characteristics of ion emission should provide a better understanding of its mechanisms, as generation of negative ions has a resonant character. To gain more insight into the phenomenon, we also plan to carry out two-channel measurements on simultaneous detection of oppositely charged particles and their mass analysis using a special ultrafast time-of-flight mass spectrometer.

Study of the mechanoemission phenomenon has both a purely academic significance for physics of polymer strength and an important value for applications in field sensors, since ionization of stressed macromolecules can affect the operation of various electronic devices [30, 31].

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