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Volatile products formed during electrical breakdown of polyethylene terephthalate and polypropylene films in high vacuum

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In this article we present the results of time-of-flight mass spectrometry of volatile products formed during the electrical breakdown of polyethylene terephthalate and polypropylene polymer films in high vacuum. During the breakdown of films, all the substance emitted from the breakdown channel is a gas of low-molecular products of destruction of macromolecules. The breakdown mass spectra do not contain lines of carbon molecules, the presence of which could indicate carbonation of the channel. To explain the formation of charge carriers, the ionization mechanism of destruction of macromolecules in an electric field is used without the involvement of impact ionization. The final stage of electrical breakdown (the flow of a high-density conduction current) occurs when the critical concentration of traps and electrons $\approx 10^{24}\,\mathrm{m}^{-3}$ is reached.

Keywords: electrical breakdown, mass spectrometry, thermodestruction, ionization, macromolecule, trap.

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Introduction

Polymer dielectrics are in great demand as insulators in electronics and for creating means of electrical energy transmission. This is the reason for the study of their electrical strength. Despite the long history of such studies, the physical mechanisms of the electrical breakdown of polymer dielectrics are not well understood. In particular, the reason for the high conductivity of the polymer being a basis of high current densities in the breakdown channel is unclear [1]. Previously, it was supposed that the reason for the high conductivity lies in the carbonization of the breakdown channel [2,3]. However, it is obvious that the carbonization process cannot proceed without significant heating of the polymer, i.e., the electric current is the primary one.

The study of the chemical composition of the products formed in the breakdown channel can help clarify the above questions. Usually, experiments on the breakdown of dielectrics are carried out at normal atmospheric pressure. The presence of various gases and liquids can effect the experiment and lead to inadequate results. In this context, it is important to note that polymers are used in technical installations operated in space. Therefore, it is reasonable to study the breakdown in a vacuum. However, there are few publications in this area. Extensive studies have been carried out on the processes of electrical breakdown of vacuum gaps [4]. Surface discharges on dielectrics, including those on polymeric surfaces under vacuum conditions, were studied in [5]. We know the only paper related to the breakdown of polymer films at a pressure of 10^{-8} Torr [6]. This paper describes the study of the breakdown of polytetrafluoroethylene (PTFE), polyimide (PI), and polyethylene terephthalate (PET) using the TOF mass spectrometer. The thickness of the films did not exceed $100\,\mu$m. During the breakdown, low molecular fragments were mainly registered: CO and CO_2, as well as light hydrocarbons. In the opinion of the author, the reason for these molecules formation is related to the action on the monomer of the electron beam of the ion source. As a consequence, this leads to the fragmentation or modification of oxygenated functional groups. Note that the spectrum of volatile substances did not contain mass-spectral lines of carbon molecules. This paper is mostly descriptive and does not contain conclusions related to the mechanism of electrical breakdown.

In this paper it is necessary to clarify the role of carbonization during the breakdown. It is important to compare the pressure burst during the breakdown with the pressure that could be provided by the volatile products that make up the volume of the hole formed during the breakdown. This will make it possible to draw conclusions regarding the phase composition of the material ejected from the polymer upon breakdown. Additionally, it is expedient to obtain mass-spectra of the thermodestruction of polymer films and compare them with breakdown spectra at a constant electron energy in the ion source, since under conditions of ultrahigh exposure speed the physical and mechanical properties of polymers can change [7,8]. On the basis of the data obtained and with the involvement of earlier results propose a picture of the development of the process of the electrical breakdown of the polymer and support it with calculations of the accumulation of charge

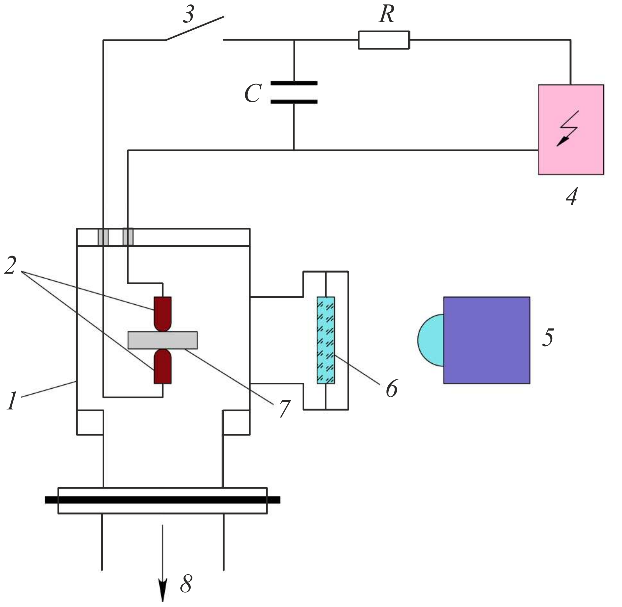

Figure 1. Scheme of the experimental setup: *1* — vacuum chamber, *2* — electrodes, *3* — key, *4* — voltage source, *5* — photo camera, *6* — window, *7* — sample, *8* — mass reflectron.

carriers and traps with the time of application of the electric field.

1. Experimental procedure

The objects of study were PET capacitor films ($10\,\mu$m thick) and polypropylene (PP) films $6\,\mu$m thick. The choice of the PET film made it possible to compare our results with the data presented in the paper [6]. As for PP, a significant difference in the properties of PET and PP films seems to be very important when comparing the results of mass-spectrometry of the studied films.

The experimental setup is shown in Fig. 1. The volume of the vacuum chamber was $V \approx 20\,\mathrm{l}$. A high vacuum was obtained using a turbomolecular pump. The residual gas pressure was at the level of $\sim 5 \cdot 10^{-7}$ Torr. The polymer film was fixed between tungsten cylindrical electrodes 2 mm in diameter. At the point of contact with the sample the electrodes had the shape of a hemisphere with a radius of 1 mm. One electrode was grounded, the other served as an anode. A capacitor with capacitance $C = 300$ pF was charged through limiting resistance $R = 40\,\mathrm{M\Omega}$. For breakdown the measuring cell was connected to the preliminarily charged capacitor. On average the breakdown voltage was 2600 V for PP and 3800 V for PET. The breakdown was visually observed through the quartz window of the vacuum chamber.

The mass composition of positive ions was measured using an MCX-6 mass reflectron [9,10] and DPO4034 Tektronics$^{\mathrm{TM}}$ digital oscilloscope with a point density of $\sim 10^6$ per spectrum in the mode of spectra averaging with 512 averages. The spectra were formed at an energy of ionizing electrons 100 eV. The distance from the polymer sample to the ionization region was ~ 40 cm. In the breakdown experiments the total pressure was monitored using the 972B Dual Mag$^{\mathrm{TM}}$ (Pirani/cold cathode) digital pressure gauge connected to the mass-spectrometer. The pressure measurement was synchronized with the registration of mass-spectra. Spectra formed during the thermal destruction of polymer films in vacuum at 673 K were also obtained. The spectrum registered during thermal degradation was obtained by smooth heating of the bulk polymer sample attached to a tantalum heater substrate. The substrate was resistively heated by electric alternating current at a rate of 50 K/min.

2. Results and discussion

The breakdown of PET and PP films was accompanied by a blue flash. In some cases, plasma jets were clearly visible (Fig. 2). As a result of the breakdown a hole was formed in the films. Fig. 3 shows photo of the hole formed during the breakdown of the PET film. The breakdown was accompanied by a burst of total pressure lasting for ~ 1 s (upper inset in Fig. 4). The maximum level of pressure peaks was $(2{-}4) \cdot 10^{-6}$ Torr, their duration was about $\Delta t \approx 0.1$ s. The pressure recovery time at the used pumping speed $v = 100$ l/s was about 1 s. The short pressure bursts recorded during the breakdown can be explained by the non-stationary nature of the breakdown process, as well as by the high speed of the plasma outflow.

Fig. 4. shows the mass-spectra recorded during the breakdown (curve above, shown by the red line (in the online version)) and during thermal destruction (curve below, shown by the blue line (in the online version)) for PET. The results for PP are presented in Fig. 5. The thermal degradation spectra were obtained by subtracting the background spectrum before heating from the typical spectrum recorded during heating and at total pressure $P \sim 10^{-5}$ Torr. Above 473 K, lines of degradation products of macromolecular chains are recorded in the spectrum

Figure 2. PP film breakdown photo.

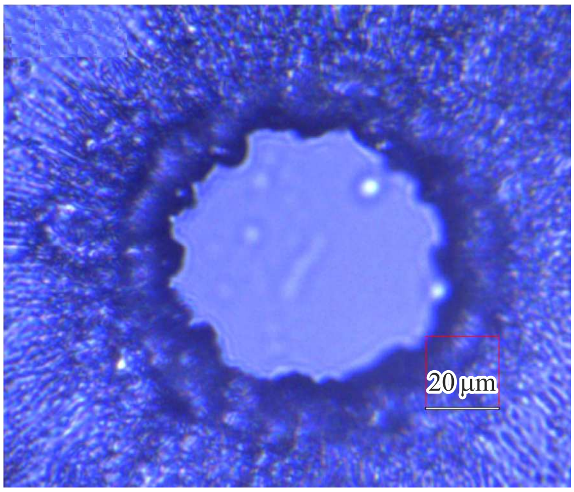

Figure 3. Photo of the hole formed during the breakdown of PET film.

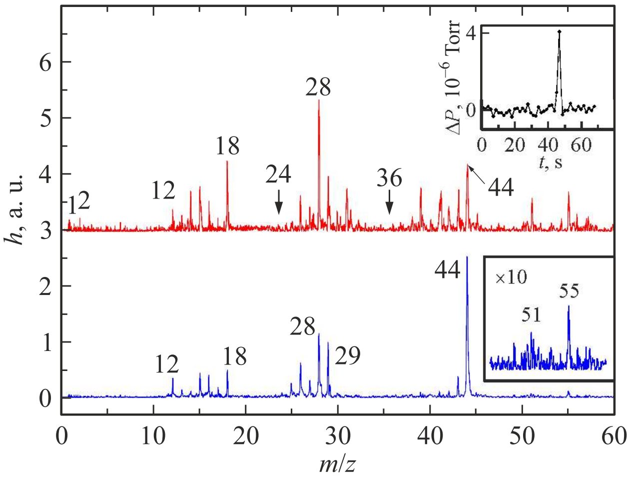

Figure 4. Mass-spectra recorded during the breakdown of the PET film (upper spectrum) and during heating (lower spectrum, temperature $\sim 673\,\mathrm{K}$). The inset at the top shows the dependence of the total pressure in the device chamber in the breakdown experiment. The arrows on the spectrum during breakdown show the position of the possible lines C_2^+ ($m/z = 24$), C_3^+ ($m/z = 36$).

of residual gases, the interpretation of their composition makes it possible to identify lines that agree with the mass-spectra characteristic for the main thermal degradation products of PET [11]: carbon monoxide ($m/z = 28$, 16, 12), carbon dioxide ($m/z = 44$, 28, 16, 12) and aldehyde ($m/z = 29$, 44, 43, 15). The intensities of the spectral lines corresponding to other possible PET degradation products (benzene, bisphenol) are at the noise level. So, the mass-spectra are the sum of the mass-spectra of carbon oxides and aldehyde.

In experiments on the breakdown of polymer films the total pressure in the vacuum chamber Δp had a pulse character at the moment of breakdown (upper inset in Fig. 4, 5). Synchronization of the spectra recording and the recorded total pressure in the device chamber made it possible to record the spectrum corresponding to the maximum pressure burst shown in the inset. The spectrum shown at the top in Fig. 4, 5 is the difference between the spectrum at the maximum of the pressure burst and the background spectrum before breakdown. On the lower spectrum an enlarged view shows a section of the thermal destruction spectrum in the range $m/z = 48-60$, also obtained by subtracting the spectrum during thermal destruction and the background spectrum before heating the sample. The thermal destruction spectrum was obtained at the same sensitivity of the device, but at a higher (~ 10 times) partial pressure of the destruction products as compared to the magnitude of the pressure jump during breakdown. For example, in the spectrum of PET breakdown there are 51 and 55 background lines, which are also present in the thermal degradation spectrum (this region is shown enlarged in the thermal degradation spectrum in Fig. 4), but they have a lower relative intensity due to the significantly smaller contribution of partial pressures of polymer degradation products in the full spectrum during breakdown. A comparison of the spectra shows that the breakdown spectrum contains almost all lines of thermal degradation products. The line with $m/z = 12$ represents the CO and CO_2 fragment ions. This line, in principle, can contain the contribution of the ion C^+, formed during the ionization of the carbon atom, which can appear during graphite sublimation [12,13]. However, during graphite sublimation [12], the intensity of the ions C_2^+ ($m/z = 24$), C_3^+ ($m/z = 36$) is expected to be comparable to the intensity of the ion C^+. In our experiment, the intensity of the lines C_2^+ ($m/z = 24$), C_3^+ ($m/z = 36$) is at the noise level (Fig. 4, 5). In view of the absence of the lines C_2^+ and C_3^+ in the breakdown spectra, the most probable cause of the pressure burst in the vacuum chamber during breakdown is the formation of degradation products in composition close to the products of thermal degradation of the polymer. The thermal

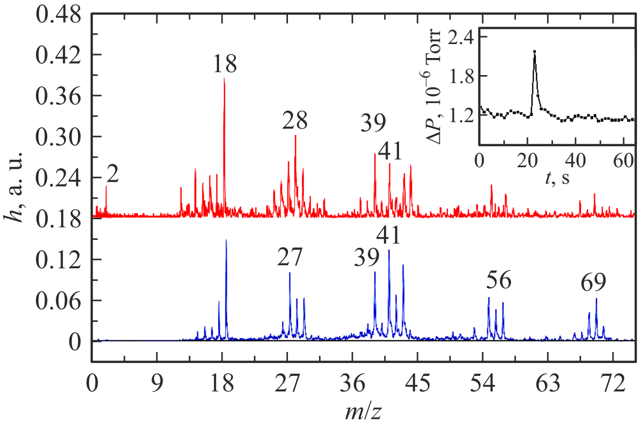

Figure 5. Mass-spectra recorded upon breakdown of the PP film (upper spectrum) and upon heating (lower spectrum, temperature $\sim 573\,\mathrm{K}$). The inset at the top shows the dependence of the total pressure in the device chamber in the breakdown experiment.

degradation spectrum of PP during heating indicates the presence of saturated and unsaturated hydrocarbons in the products, for example, propylene ($m/z = 41$, 39, 27) and cyclohexane ($m/z = 56$, 41, 84, 69). The comparison of the spectra also shows that the breakdown spectrum contains almost all lines of thermal degradation products, but with a different ratio of lines.

Note that, during breakdown the low-intensity signals are recorded in the region of the lines H_1^+ ($m/z = 1$) and H_2^+ ($m/z = 2$). Their analysis is still difficult because of their extremely low intensity. But it is obvious that the carbonization of the polymer must be accompanied by the evolution of hydrogen, the lines of which in the mass-spectrum must be quite intense. In general, the ratio of the intensities of the lines of the breakdown spectra can be determined by the impulsive nature of the action on macromolecules of fields of various nature, which can change both the properties of macromolecules and the mechanism of their decay. In this connection, in contrast to the case of thermal destruction, the interpretation of specific products of the of macromolecules degradation during breakdown was not yet carried out.

Note that the polymer breakdown data obtained with the mass-spectrometer indicate that volatile products are not a consequence of the destruction of the carbonized conductive channel.

The change in pressure Δp upon breakdown can be estimated by assuming that the polymer weight with density of ρ corresponding to the volume of the formed channel is converted into gas with molecular weight of μ. In this case, you can use the ratio:

$$\Delta p = kT\, N_a\, \frac{\rho}{\mu}\, \pi r_0^2\, \frac{d}{V_c}, \tag{1}$$

where $k = 1.38 \cdot 10^{-23}$ J/K is the Boltzmann constant, temperature $T = 300$ K, $N_a = 6.02 \cdot 10^{23}$ 1/mol is the Avogadro number, $\mu = 20 \cdot 10^{-3}$ kg/mol, $\rho = 1400\,\mathrm{kg/m^3}$ (for PET), breakdown channel radius $r_0 = 25 \cdot 10^{-6}$ m, polymer film thickness $d = 10 \cdot 10^{-6}$ m, effective volume of vacuum chamber $V_c \approx 10$ l, $V_c \approx V - v\Delta t$. Calculations by formula (1) show that for a breakdown channel diameter of $40-50\,\mu$m and film thickness of $10\,\mu$m, the number of particles with the weight of 20 a.m.u., ejected from the channel corresponds to experimentally observed pressure burst, i.e., $\Delta p \approx (2-3) \cdot 10^{-6}$ Torr. This compliance leads to the conclusion that the material inside the breakdown channel is converted into a low molecular gas. In this case, high pressure develops in the breakdown channel, which significantly exceeds the strength of chemical bonds in macromolecules. The processes that occur during the electrical breakdown of solid dielectrics at the stage of high-density current flow through the breakdown channel are similar to the processes during the electrical explosion of conductors. When a conductor explodes, the pressure develops up to 480 MPa [14]. The pressure in the channel can be estimated very approximately by formula (1) if we assume that the chamber volume in it is set equal to the volume of the hole in the film. Then, for example, for $T = 800$ K we get $\Delta p \approx 465$ MPa. As can be seen, in any version of the calculation the pressure developed in the channel significantly exceeds the strength of PET, which is 140 MPa [15]. The ejection of material in the molten state cannot lead to the observed pressure burst and cannot ensure the formation of the mass-spectrum. The strong similarity of the spectra during breakdown and thermal degradation indicates the breaking of chemical bonds and the formation of low molecular products in both cases.

At present, there is no common understanding of the physical mechanism of the intermittent transition from the first stage of polymer destruction, which is associated with the destruction of macromolecules initiated by the electric field, to its final stage, i.e., destruction of the sample. However, it was established that the conducting channel is formed in the sample during the time interval $\sim 10^{-9}$ s. This channel is capable of conducting high currents, which leads to the destruction of polymer dielectrics, i.e., to the formation of a through hole (Fig. 3). The data obtained indicate that the high conductivity in the polymer is due to other factors but not to carbonization. The high current density in the polymer can be a consequence of both increasing of the concentration of charge carriers, i.e., electrons and holes (positively charged ions), and increasing of their mobility.

Electrical breakdown is often explained by impact ionization. However, due to the short free path of the quasi-free electron this process in dielectrics is difficult. The electron cannot acquire the energy equal to the ionization potential of macromolecules ξ in the solid phase. For PET $\xi = 7.35$ eV, for PP $\xi = 8.65$ eV [16]. Besides, in thin-film capacitors the operating voltage can be even lower than the ionization potential. Therefore, the ionization mechanism for the electrical breakdown of polymers was proposed. According to this mechanism, in a strong electric field the ionization of molecules occurs as a result of electron tunneling transitions from HOMO to LUMO and to traps [17]. Field ionization of macromolecules is possible not only in the volume of polymer dielectric, but in the immediate vicinity of the anode. The process of formation of positively charged molecular ions in the immediate vicinity of the anode due to the tunneling transition of electrons from the HOMO level of the macromolecule to free electronic levels in the metal can be considered as the injection of holes into the polymer. This process was analyzed in detail in [18]. The electric field lowers and narrows the potential barrier for electrons. The decay of macromolecules that lost the electron is accompanied by the formation of macroions and free radicals, which react with molecules. These processes lead to the formation of atomic groups with a positive electron affinity, i.e., deep electron traps. The appearance and accumulation of traps in a strong electric field accelerates the formation of macroions in the polymer, since it becomes possible for the electron to tunnel from the HOMO level of macromolecule into a deep trap. Breakdown occurs when the critical concentration of traps and electrons is reached. The method for calculating the concentration of macroions and electron traps in the polymer in a strong electric field is given in papers [17,19]. Using this method we calculated the time dependence of the total concentrations of positive molecular ions for PET and PP. The necessary data for ionization potentials and electron affinity were taken from [16]. Fig. 6 shows a graph of the traps concentration increasing in the field with strength $F = 18 \cdot 10^8$ V/m for PET. The curve of the concentration increasing of macroions (and electrons) practically coincides with the curve of traps accumulation. For PP the curves are similar. It can be seen that the breakdown is characterized by an avalanche-like concentration increasing of both traps and current carriers. In general, the presence of traps in the polymer is the basis for creating electrets. A noticeable mobility of charge carriers would prevent the accumulation of charges. However, to conduct the appreciable electric current the charge carriers must have a sufficiently high mobility. Up to the final moment of breakdown the polymer remains a dielectric. This state can last for a long time, even a very long time, depending on the level of the applied field. Over time the number of traps becomes very large, and the distance between them decreases. The electrons concentration also increases greatly, as ionization continuously occurs. Since electrons and positive ions accumulate at the same time, the resulting solid-state plasma remains electrically neutral. Upon reaching a high concentration of solid-state plasma, the ionization potential of molecules decreases due to Debye screening [20]. An avalanche-like process of concentration growth of electrons and traps begins. The increasing of the traps number leads to increasing of the permeability of the potential barrier, i.e., the mobility of charge carriers increases. At a high concentration of traps the individual energy level in any of the traps can turn into a zone [21]. The polymer acquires almost metallic conductivity. The first stage of the breakdown, i.e., the accumulation of charges, was completed. The next stage of the breakdown begins, breakdown as such, which is characterized by the current flow through the breakdown channel for a time interval of less than 1 ns. The instantaneous heat source oriented perpendicular to the film occurs. A cylindrical heat wave begins to move from this channel, causing the destruction and evaporation of the material. High pressure is created in the channel. As a consequence, the material is ejected from the heated region. This is a dynamic process that proceeds with the hole formation in the film, the hole has hot walls and is filled with gas. When the pressure in the channel decreases, Paschen's law is fulfilled, and ordinary gas discharge occurs. Glow during the breakdown can also be caused by the recombination of electrons and holes in the solid-state plasma when current flows through the channel, and the subsequent ejection of luminous plasma in the form of jets, clearly visible in the photos (Fig. 2). The electrical breakdown of the polymer is completed. As can be seen from Fig. 6, the critical concentration of traps is $\geq 10^{24}\,\mathrm{m}^{-3}$. Note that there are papers that discuss the role of electron traps in polymers during breakdown [22–24]. This determines the interest in studying the nature of their formation, as well as other properties, for example, energy distribution.

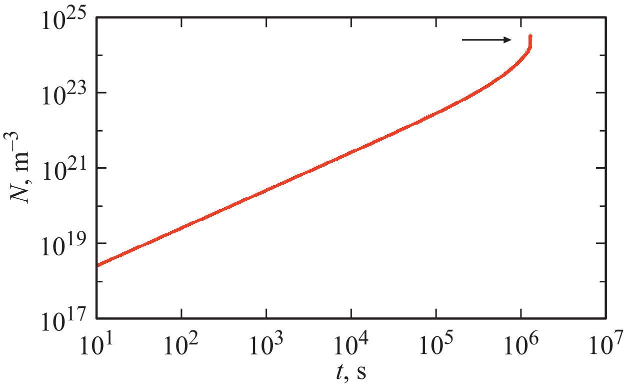

Figure 6. Concentration of traps N for PET on time t at an electric field strength $F = 18 \cdot 10^8$ V/m. The arrow shows the final stage of the breakdown.

Since the electrical breakdown of polymers is accompanied by plasma ejection into the vacuum chamber, the question may arise about the plasma ions effect on the readings of the ionization pressure gauge, and about the adequacy of the interpretation of the recorded pressure bursts during breakdown. It is known that in the used pressure gauge with a cold cathode at a pressure of about 10^{-6} Torr, the ion current is $1\,\mu$A [25]. It is possible to make a comparative assessment of this current with the current created by positive ions from the breakdown channel at the location of the pressure gauge. Let us assume that the distance from the breakdown place to the pressure gauge is L, and the radius of the pressure gauge is R_m. Under the condition of isotropic angular distribution of emitted particles, the particles flux attenuation coefficient will be

$$K = \left(\frac{R_m}{L}\right)^2. \tag{2}$$

A bright flash, that accompanies the breakdown, indicates the recombination process. In time t_0 the concentration of particles will decrease to a value [26]:

$$N_0 = \frac{N}{1 + N\beta t_0}. \tag{3}$$

According to the pressure gauge passport, its response time is $\tau = 0.1$ s. For the plasma current we can write the expression

$$I_0 = \pi d r_0^2 \frac{N_0 K e}{\tau}. \tag{4}$$

For $L = 0.44$ m, $R_m = 14$ mm, $\beta = 10^{-13}\,\mathrm{m}^3/\mathrm{s}$, $e = 1.6 \cdot 10^{-19}$ C, $N = 10^{24}\,\mathrm{m}^{-3}$, and $t_0 = 10$ ns we get $I_0 \approx 3.2 \cdot 10^{-8}\,\mu$A. A ion with the weight of 20 amu and energy of 3 keV will fly a distance of about 1.7 mm in 10 ns. At longer times, recombination will be difficult. Here, the fact that the placement geometry of the discharge cell and the pressure gauge precludes direct entry of particles into the pressure gauge is still not taken into account. Besides, since the radius of the conducting channel r_0 is not exactly known, we equate it with the radius of the hole. However, it is clear that as r_0 decreases, the current I_0 becomes smaller. Thus, $I_0 \ll 1\,\mu$A and, therefore, in the setup used the ions escaping from the breakdown channel of the polymer cannot affect the pressure gauge readings.

Conclusion

Thus, it was shown that during the breakdown of polymer films in vacuum, the material ejected from the breakdown channel is a gas of low-molecular products of the macromolecules destruction. It was established that the compositions of products during thermal destruction and electrical breakdown qualitatively coincide. The breakdown mass-spectra do not contain lines of carbon molecules and intense lines of hydrogen. Otherwise, this would make it possible to explain the low electrical resistance of the channel by carbonization. Consequently, the reasons for the high breakdown current density are a significant concentration of current carriers and their mobility, which are achieved in a very short period of time as a result of the avalanche-like development of the following processes:

1) ionization of macromolecules without impact ionization under the action of an electric field narrowing the potential barrier for electron tunneling HOMO−LUMO and HOMO−trap;

2) the destruction of ionized macromolecules and the formation of macroions and free radicals that react with molecules, resulting in the formation of atomic groups with positive electron affinity, which act as electron deep traps;

3) appearance and accumulation of traps in a strong electric field accelerates the formation of macroions in the polymer, since it becomes possible for the electron to tunnel from the HOMO level of macromolecule into a deep trap. The probability of ionization increases due to the ionization potential of molecules decreasing as a result of the Debye screening in non-ideal plasma;

4) when the critical concentration of traps and electrons ($\geq 10^{24}\,\mathrm{m}^{-3}$) is reached, the probability of electron tunneling between traps increases, which causes abrupt increasing of the electron mobility.

The current flow through the breakdown channel can, in principle, lead to charring (especially in the atmosphere) and leave traces on the walls of the hole. However, this process is not a key process for the development of electrical breakdown itself and should be considered as a consequence of the breakdown. In this sense, it is important to study the role of the capacitor C (Fig. 1) in the formation of a hole in the film and the occurrence of secondary processes, such as carbonization and radio emission.

A more detailed study of electrical breakdown requires measurements of mass-spectra with a higher time resolution and the spectrum of the luminescence formed during the polymers breakdown in vacuum and the time parameters of the luminescence flash. It is also important to carry out calculations of thermal problems in order to relate the results of these calculations to the moment of hole formation in the polymer. These works will expand our knowledge in the field of electrical destruction of polymers and provide methods for creating strong insulating materials for electrical engineering.

Conflict of interest

The authors declare that they have no conflict of interest.

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