



ACCUMULATED PROCESSES IN KINETIC OF MECHANICAL AND ELECTRICAL DESTRUCTION OF POLYMERS

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Abstract

The distribution on longevity τ -time of waiting of bursting (mechanical destruction on constant tension) and punching (electrical destruction on constant intensity of field) of polymer films of polyethyleneterephthalate and polyethylene was measured. The results of uninterrupted experiments and experiments with interrupting the influence of load on samples, remained whole after tested within a time, answering the average value of $\lg \tau$ were compared. The duration of interval, temperature, tension of field of opposite sign, depending on what was observed the various degree of regeneration of durable properties of polymer objects, varied in the intervals. For the mechanical destruction it was displayed the irreversibility of accumulated changes, which were identified as fluctuation break of tense chain molecules. The capability of accumulated changes to regeneration (up to complete) was determined for the electrical destruction. This permits to connect the kinetics of electrical destruction with the formation of time of volumetric electronic charges, on achieving the initial value which begin with punching.

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1. Introduction

Break of sample under the influence of applied mechanical load and punching of sample under the influence of electrical field are of final acts developing in loaded objects of processes, preparing the approach of macroscopic loss of solidity. It is testified by numerous of experimental data on observation of so called "delayed destruction", when after the application of some constant load (mechanical or electrical) the break or punching of sample begin not immediately, but after some lapse of time, the duration of which depends on the size of load, as well on a number of factor (temperature, structural state of object, external medium, radiation influence, e.t.c.) (V. R: Regel, A. I. Slutsker, E. E. Tomashevskiy, 1974-S. N. Koykov, A. N. Tsikin, 1968). The time of waiting of break (punching) is adopted to call the durability τ . It is natural to conclude that during this time in loaded object the changes take place, the processes develop, which bring to complete loss of stability of the object to influence of load. So, the striation appears not as a critical event, but as a kinetic phenomenon.

The investigation on kinetics of destruction is carried out as by phenomenological (depending τ on mechanical tension σ or on tensivity of electrical field E , as well temperature T), and as well as by the numerous direct physical methods (V.R: Regel, A. I. Slutsker, E. E. Tomashevskiy, 1974-S. N. Koykov, A. N. Tsikin, 1968). In corresponding zones of temperature were determined the mechanisms of elementary acts: thermofluctuation (above-barrier) and tunnel (under-barrier) (V.R: Regel, A. I. Slutsker, E. E. Tomashevskiy, 1974-R.L. Salganik, A. I. Slutsker, Kh. Aydarov, 1984- M. S. Dakhiya, V. A. Zakrevskiy, A. I. Slutsker, 1987). The questions of reversibility and irreversibility of elementary processes, preparing the break (punching) of body are of great importance.

2. Materials and Methods

The elucidation of degree of reversibility of accumulated processes in kinetics of mechanical and electrical destruction of a number of polymers was carried out in the present work. For the objects of investigation were taken the films with thickness in some ten micrometers from the nonoriented amorphous-crystalline polymers: polyetheleneterephalate (PETPH) and polyethylene (PE).

The time of waiting of break of samples in influence of stretching mechanical load (mechanical longevity τ_m) and for such kind of samples - time of waiting of punching in influence of constant electrical field (electrical longevity τ_e) was measured in the experiments.

The mechanical longevity was measured in the bursting equipment, keeping up the constancy of given tension in extension of sample) (V. R: Regel, A. I. Slutsker, E. E. Tomashevskiy, 1974). The electrical longevity was measured in the cell with pressed polished electrodes. The punching was fixed according to impulse of current in the chain.

Elucidation the degree of reversibility of accumulated processes, leading to destruction was carried out on the basis of known way - on comparison the result of measuring of longevity in uninterrupted influence of load (both the mechanical and the electrical) with the results of measuring of longevity in interrupted influence of load. The result of experiments of the same type for mechanical destruction of solid bodies, including the polymers, are described in) (V. R. Regel, A. I. Slutsker, E. E. Tomashevskiy, 1974- S. N. Zhurkov, B. N. Narzullayev, 1953). However, it should be marked that the quantitative analysis the results of experiments was carried out without proper calculation of the static of longevity.

The same experiments for the electrical destruction were carried out on ceramics, which the statistics of longevity was taken into account more strictly (M. S. Dakhiya, V. A. Zakrevskiy, A. I. Slutsker, 1969). The existence of enough strong scattering the value of longevity for externally identified samples, bursting or punching in given values σ or E and keeping up the identical influence conditions of load (temperature, medium) is characteristic in the study of longevity of polymers (as well as for other materials). Therefore, the measuring with interrupting of influence of load on single samples can not give the clear answer. At present work the measuring of τ was carried out on series of 30 samples and was analyzed the functions of distribution of samples on longevity.

3. Results and Discussion

Integral functions the distribution of samples of PETPH lg τ in corresponding σ , E and T are given in the Fig. 1. The function $1 - n_\tau / n$, where n - full number of samples in series; n_τ - number of samples, remained whole after the time of endurance of τ is laid according to the axis of ordinates. as it is obvious, the diagrams of these functions for τ_m and for τ_e have uniform S-form with effective width of distribution $\Delta \lg \cong 1/1,5$. The form of distribution is close the normal distribution of accidental values (integral probability). The width of distribution was conditioned, evidently, by variation of structure and defectiveness of samples, micro-roughness of electrodes, e.t.c.

The values of longevity $\tau_{1m}=760c$ and $\tau_{1e}=660c$, answering the destruction of the half of number of samples are defined from the Fig. 1. Then was taken new series of the same samples and they bore in the same values of σ , E and T during the time of τ_{1m} and τ_{1e} correspondingly, after of which the load (σ or E) was taken away. As a result, half of the number of samples remained indestructed, with which the further operation were carried out.

The sense and way of analysis of data are explained schematically in the Fig. 2. Here the Curve 1.- upper part of curves distribution of the Fig. 1, i.e. constructed from the level 0,5 in Fig. 1 and renormalized in whole number remained indestructed samples of accumulated samples (with ordinate $1 - n_\tau / 0,5n$). Let us think that after the bearing under the load during the time of τ_1 in remained destructed samples of accumulated changes during the time of interval were melted (full regeneration), then after the secondary application of the same load distribution of these samples on the secondary longevity must coincide with the Curve 1. If after

the bearing of τ_1 and taking down the load of accumulated changes is completely reserved during the interval, then the distribution of samples on secondary longevity must be obtained by the help of reconstructing the Curve 1 from values on $\lg \tau$ to values $\lg (\tau - \tau_1)$ and take the from of Curve 2 (Fig. 2), I. e. pass through the zone of lesser values of τ , particularly in the zone of initial (lower) part of distribution. Finally, if in interval between the taking down of load and its secondary application in samples passed the partial regeneration of accumulated changes, then the distribution of samples on secondary longevity must pass between the Curve 1 and 2, i.e. must correspond the Curve 3.

Let us take notice to the results of experiments with interrupting of the influence of load. Distributions of longevity in unbroken influence of load for samples of PETPH with longevity, exceeding the $\tau_{1m}=760c.$ and $\tau_{1e}=660c.$, i.e. renormalized from at 0,5n upper parts of curves distribution (Fig. 1) are presented in the Fig. 3a, 3b by Dots 1. Dots 2-results of reconstructing the Dot 1 on coordinate $\lg (\tau - \tau_1)$. Dots 3- experimental data on secondary longevity after the bearing of samples under load during the time of τ_1 and interval the influence of load (10^4 with $T=123$ K for mechanical destruction and $1,8 \cdot 10^4$ with $T=153$ K for electrical destruction). The nearness of Dot 2 and 3 in the Fig. 3a, 3b testifies the fact that during the first bearing under the load τ_1 in samples were accumulated the changes which reserved in the interval of influence of load in the same temperatures in which the load influenced and brought to more lower values of secondary longevity. So, in the given stage of investigation for PETPH the regularity of kinetics both the mechanical and the electrical destruction turned out to be uniform. The corresponding data for PE are the same. I. e. in conditions of kinetics of mechanical and electrical destructions in comparatively lower temperatures the accumulated changes in both cases appear as irreversible.

Now let us consider the experiments when during the interval (taking down the load) we shall change the influence on samples. For mechanical destruction during the time of "rest" the samples were born in high temperature. The results of such experiments, when interval the unloaded samples of PETPH were born in 323 K during 10^3 c., are given in the Fig. 4 (Dots 3). It is obvious that the increase of temperature of "rest" did not bring to change the distribution of samples on secondary longevity. I. e. regeneration of changes are not observed. It permits to conclude that the changes given rise the influence of mechanical load are enough stable.

Two forms of influences were used for electrical destruction during the "rest": as in the previous case, increase of temperature, as well superimposition on sample of constant electrical field of opposite sign (opposite field). The result are presented in the Fig. 5.

Distribution of samples of PETPH on secondary longevity, when during the interval of the influence of electrical field the samples bore in 333 K within 10^3 c., is given in the Fig. 5a (Dots 3). It is obvious that the remove of distribution to the side of increase of secondary longevity took place. In accordance with sense of Curve 3 in the Fig. 2 this means a definite degree of regeneration of changes in samples of PETPH.

The influence of opposite field on secondary longevity of PETPH is shown in the Fig. 5b. It is obvious that regeneration of accumulated changes takes place here during the time of "rest". By this it is possible to make the regeneration practically full (Dots 4 in the Fig. 5b).

So, essential difference in the character of accumulating under load changes for mechanical and electrical distractions of polymers was brought into light: irreversible for mechanical and irreversible for electrical.

A question on the degree of reversibility of changes, leading or preparing the macroscopic destruction of loading bodies is of interest from the point of view of both the science and the techniques. From the standpoint of physical plan it permits to judge more detailed about the elementary processes, preparing the destruction. For techniques it means to be prolonged the efficiency of constructions.

The irreversibility of accumulated changes in mechanical destruction of polymers previously (V. R: Regel, A. I. Slutsker, E. E. Tomashevskiy, 1974- S. N. Zhurkov, B. N. Narzullayev, 1953) is confirmed in the given work. It makes agree well with the idea about accumulation with the time of chain molecules. Just the act of break of mechanical tense chain molecule, realized by fluctuation mechanism, appears as an elementary act restricting the polymers (V. R: Regel, A. I. Slutsker, E. E. Tomashevskiy, 1974). And further process for destruction of polymer develops on the basis of such molecular breaks: formation of embryonic cracks, their accumulation, growth, blending, formation of main cracks and break of total sample (V. R: Regel, A. I. Slutsker, E. E. Tomashevskiy, 1974).

It is of interest that the recombination of break of chain molecule is hardly probably, as after the break of secondary freely radical reactions, "twisting" by unloaded break the zones of molecule prevents from regeneration of its integrity (V. R: Regel, A. I. Slutsker, E. E. Tomashevskiy, 1974- V. A. Zakrevskiy, V. S. Kuxsenko, A. Y. Sabostin, 1969). Specificity of the process of destruction of polymers can be considered in this. It should be marked here that regeneration of solidity in mechanical destruction the bodies of three-dimensional atomic-molecular structure, partially, metals proves to be possible (V. I. Betekhtin, A. I. Petrov, N. K. Ormanov, 1989). By creating the corresponding conditions (temperature, pressure) it is succeeded to a marked degree to establish the initial solidity of objects ("to cure" the accumulated microcracks and pores) and by this to increase their mechanical longevity (V. I. Betekhtin, A. I. Petrov, N. K. Ormanov, 1989).

A question related to elementary acts of the process, determining the electrical longevity of polymer, remains insufficiently elucidated for the present. Available data prove that fluctuation mechanism is characteristic for these acts (M. A. Bagirov, Y. G. Rahimov, T. F. Abbasov, S. A. Abasov, 1973- V. B. Berezhenskiy, V. M. Bykov, V. V. Gorodov, (1967); various processes on electronic and atomic-molecular level are discussed (B. I. Sazhina, 1968- A. L. Robezhko, V. R. Vazhov, G. V. Efremova, 1981). The data obtained in the present work concerned to regenerativeness of the changes, accumulating of which bring to electrical destruction (punching) of polymers, permit to make some conclusions about the character of these changes at least for investigated cases. Evidently, the changes are

accumulated here only on electronic level. The molecular regrouping, breaks of molecules, obviously, do not play a significant role. The most natural is considered for being under electrical tension of polymer dielectrics, the formation in it from time to time the volumetrically charges, on achieving sufficient value, which begin the punching. The volumetrically charge can be formed both from the injected electrons (homocharge), and at the expense of inner ionization of polymer molecules in electrical field with transition of electrons from polymer molecules in intermolecular traps (V. R. Zakrevskiy, A. I. Slutsker, 1984). The detailed elaboration of electronic processes in preparation of electrical punching of polymers remains as a problem of further researches.

The results of this work is the data obtained on the basis of statistic analysis of longevity about the character of accumulated processes with confirmation the irreversibility of these processes in case of mechanical destruction and establishing the reversibility in case of electrical destruction for investigated polymer objects.

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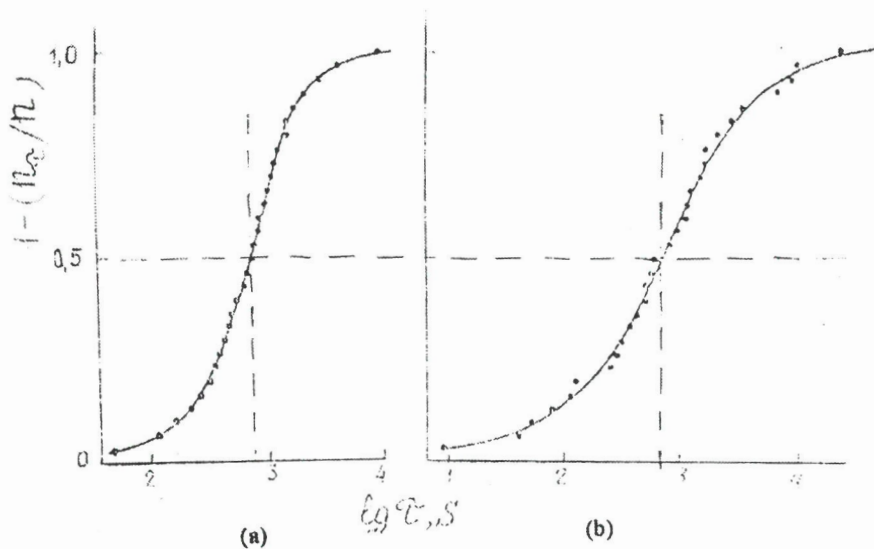


Figure 1. Integral distribution of the samples of PETPH on longevity.
 a- mechanical destruction, $\sigma=0.320$ hPa, $T=123$
 b- electrical destruction, $E=7.10^8$ V/m, $T=153$ K.

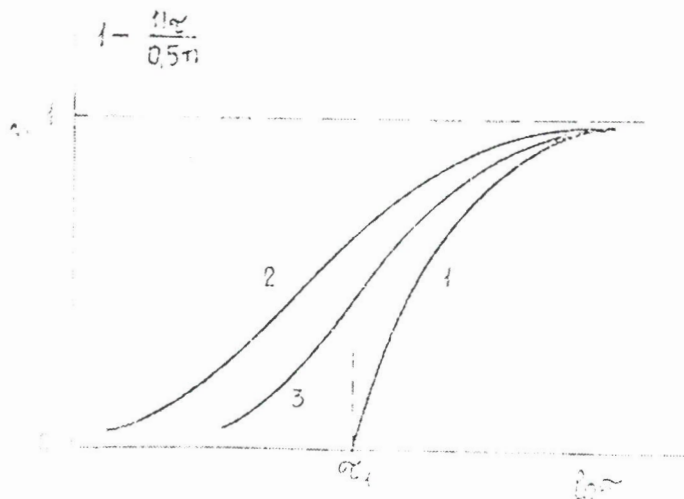


Figure 2. Diagram of the distribution of samples on longevity.
 1- destroyed during, exceeding the τ_1 ,
 2- the same distribution, but on $\lg(\tau - \tau_1)$ -on secondary longevity,
 3- distribution on secondary longevity of the same samples in their partial regeneration

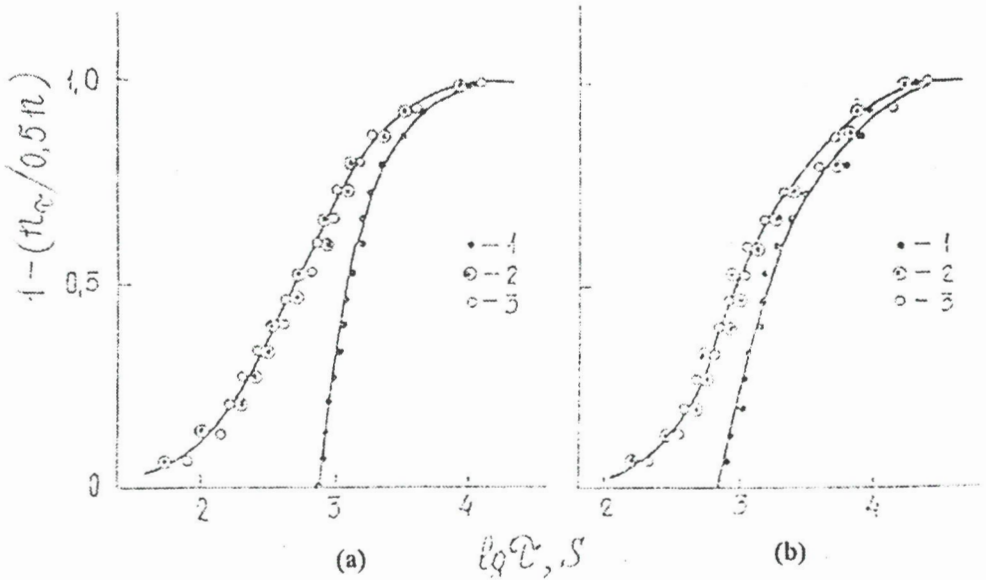


Figure 3. Integral distribution of the samples of PETPH on longevity
 a- mechanical destruction, $\sigma=0,320$ hPa, $T=123$ K; 1- destruction during, $\tau_1=760c$;
 2- distribution, $\lg (\tau-\tau_1)$; 3- measured distribution on secondary longevity after
 "rest" during 10^4c , $T=123$ K.
 b- electrical destruction, $E=7.10^8V/m$, $T=153$ K. 1- punched during, $\tau_1=660c$;
 2- distribution on $\lg (\tau-\tau_1)$; 3- measured distribution on secondary longevity after
 "rest" during $1,8.10^4c$, $T=153$ K.

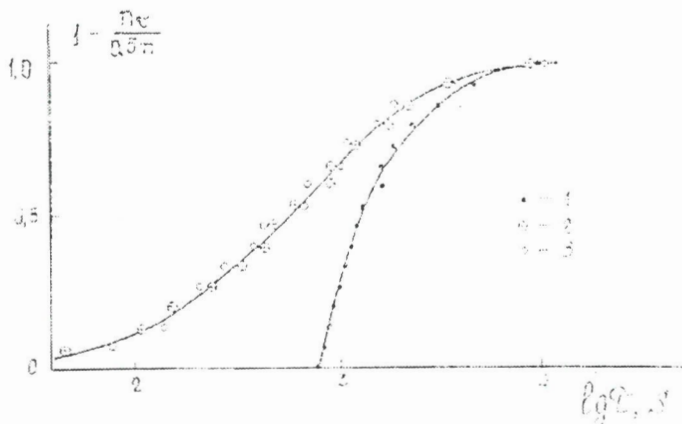


Figure 4. Integral distribution of the samples of PETPH on longevity for
 mechanical destruction, $\sigma=0,320$ hPa, $T=123$ K; Dots 1- destructed during $\tau_1=760c$;
 2- distribution on $\lg (\tau-\tau_1)$; 3- measured distribution on secondary longevity after
 "rest" during 10^3c , $T=323$ K.(absence of regeneration)

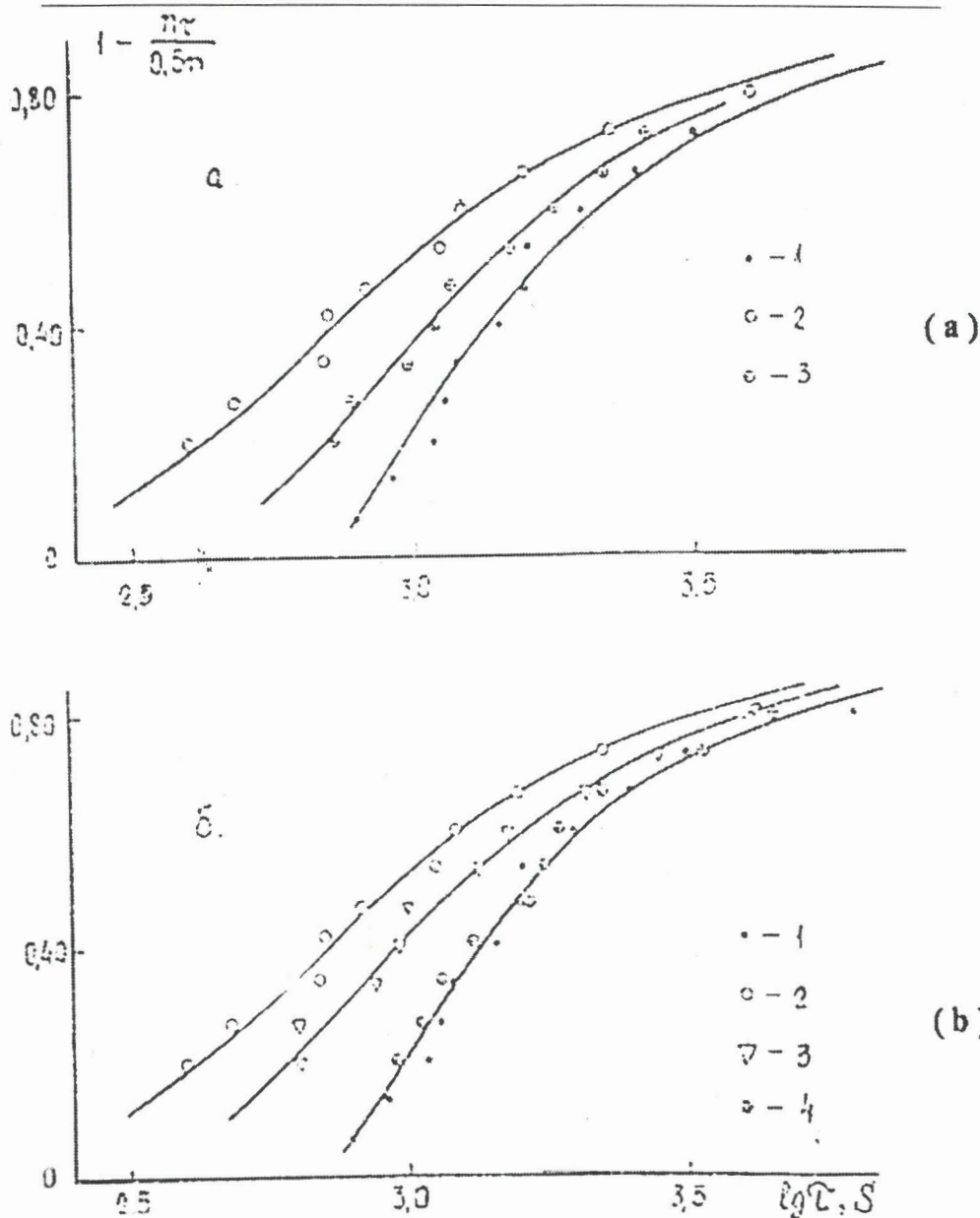


Figure 5. Integral distribution of the samples of PETPH on longevity for electrical destruction, $E=7 \cdot 10^8 \text{V/m}$, $T=153 \text{K}$.

a. Dots 1- punched during, $\tau_1=660\text{c}$; 2- measured distribution on secondary longevity after "rest" during $1.8 \cdot 10^4 \text{c}$, $T=153 \text{K}$.; 3- after "rest" during 10^3c , $T=323 \text{K}$.(partial regeneration by heating); b. Dots 1-, 2- the same that for a; 3- after "rest" during 10^3c , $T=153 \text{K}$. and action of opposite field $3.8 \cdot 10^8 \text{V/m}$; 4- after "rest" during 10^3c , $T=153 \text{K}$. and action of opposite field $5.2 \cdot 10^8 \text{V/m}$ (partial and whole regeneration by opposite field).

