

MECHANICAL FAILURE KINETICS OF POLYMER COMPOSITIONS AT MODERATE AND LOW TEMPERATURES

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The measurements of mechanical durability (rupture waiting time τ) for polymer compositions polypropylene-polyethylene of low density (PP-PELD) in temperature interval 90÷250K and at tension stress σ in interval 80÷110 MPa are carried out. The two region of $\tau(T)$ dependence are revealed at each constant σ value: well known $\tau(1/T)$ exponential dependence takes place at (~170÷250K) moderate temperatures; at low temperatures (~90÷170K) τ doesn't depend on T (temperature plateau). The conclusion to the fact that failure kinetics of polymer compositions is controlled by tunnel processes is made and the suppositions on possible tunneling mechanisms are given.

Keywords: polymer compositions, submolecular structure, electric failure, failure kinetics.

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INTRODUCTION

The conception of failure elementary acts of solids including the polymer compositions is introduced into physics of failure as a result of establishment of mechanical failure kinetic nature. The multiple systematic investigations show that failure is the kinetic phenomenon when in polymer substance the enough long process completing by the macroscopic rupture [1] develops from moment of load application.

The investigation of failure kinetics of solids at low temperatures, when the heat motion is weak and thermal fluctuations generated by it are rare ones, is in the beginning stage. The ideas on possibility of subbarrier (tunneling) mechanism of rupture of stressed interatomic bonds were given earlier [2,3]. The experimental investigations in which the dependence of failure stress on loading rate and temperature give the results coinciding with conception on tunnel rupture mechanism at corresponding low temperatures (below Debye ones) [4,5]. However, the direct measurement of temperature-force dependences of mechanical durability of polymer compositions isn't carried out.

The present paper is dedicated especially to this problem, as the registration of durability final values is the more convincing evidence of failure kinetic character and we can judge about the mechanism of failure elementary acts from temperature dependence of durability

THE OBJECTS AND MEASUREMENT TECHNIQUE

The investigation objects are optimal polymer compositions PP-PELD taken in ratio of components (PP-PELD=80:20) having different permolecular structures (PMS). The samples are taken in the form of films of thickness 20÷30 μ m. The length of working section is 10mm and width is 7mm.

The measurements of mechanical durability are carried out on tensile machine in which this or that values of temperature and tension stress are given for each sample and the time interval from load moment up to one of sample rupture is found. The sample deformation (tension) behavior during the time is also measured. The temperature is varied from ~ 90 up to 250 K. The durability is measured in time interval of several seconds up to 10⁵ ones.

RESULTS AND THEIR DISCUSSION

The temperature dependence of durability at voltage constant for slow-cooling (SC) and rapid-cooling (RC) samples of PP:PELD polymer composition are shown in fig.1.

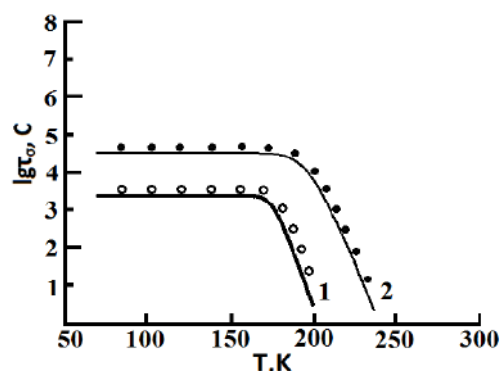


Fig. 1. Temperature dependences of mechanical durability of polymer compositions PP:PELD:
1 - SC samples, σ is 75 MPa;
2 - RC samples, σ is 85 MPa.

As it is seen from fig.1 $lg\tau(T)$ dependences for investigated polymer compositions are ones of the same type. The practical independence $lg\tau$ on T is observed in low temperature interval and this "plateau" is enough long-duration one (from 90 up to ~ 150-200 K). The

strong decrease of durability takes place at moderate temperatures. Thus, two different regions of durability temperature dependence: athermal dependence and thermosensitive one are revealed.

Let's present the obtained dependences in "hydrogen" coordinates $lg\tau - 1/T$ (fig.2) for their analysis.

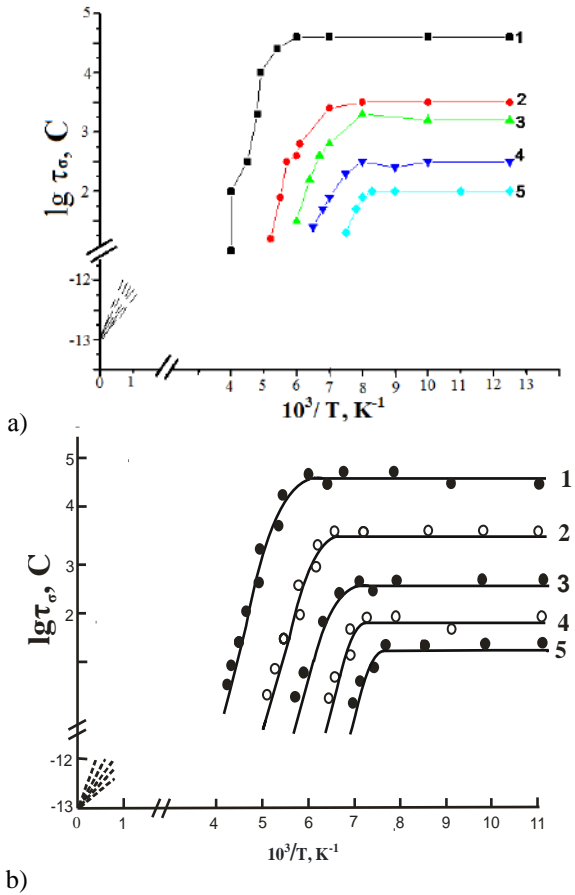


Fig.2. Temperature dependences of mechanical durability in hydrogen coordinates at different tension stress values for SC (a) and RC (b) samples of polymer compositions PP-PELD: a) 1 is 80MPa , 4 is 95 MPa , 5 is 100 MPa; b) 1 is 85 MPa, 2 is 90 MPa , 3 is 95 MPa , 4 is 100 MPa , 5 is 105 MPa.

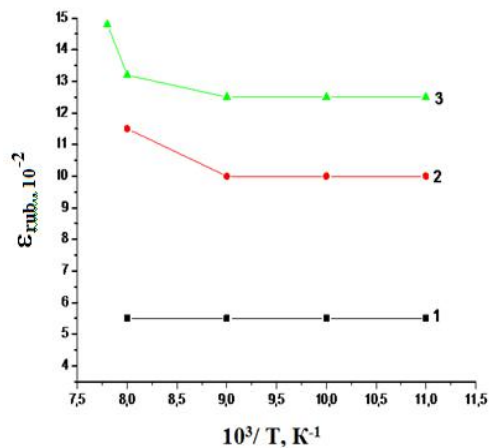
The dependences for each sample of polymer compositions at several tension stress values σ are shown (fig.2). The same two regions are revealed here: athermal and thermosensitive ones. The stress increase regularly decreases the durability in both regions. Besides, the stress influences on transition temperature from the one dependence to another: this temperature insignificantly decreases with stress increasing ("angle" on curves, fig.2). As it is seen from fig.2 $lg\tau (1/T)$ dependence has the character close to linear one in thermosensitive region for durability investigated earlier in [1]. The extrapolation of $lg\tau (1/T)$ to $1/T=0$ enough insignificantly leads to $lg\tau_{\sigma} \sim -13$ value. It gives the expression for durability in $\tau \approx \tau_{\sigma} \exp[U(\sigma)/kT]$ form.

The physical meaning is that the failure kinetics of polymer and their compositions in given temperature interval is controlled by the static waiting of rupture act of stressed skeletal bonds in chain molecules by means of subbarrier (activation, thermo-fluctuation) bond

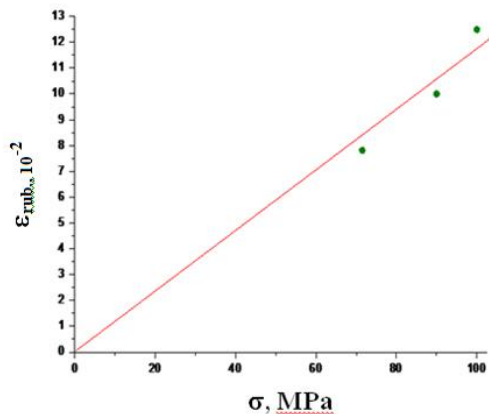
transitions from associated state into dissociated one. In low temperature interval, where the durability dependence on temperature is absent (temperature "plateau"), the durability final values, regularly decreasing with stress increasing, are the evidence of that the failure process has the kinetic character, which is accelerated by means of the stress. The absence of the temperature dependence of durability indicates that the failure thermo-fluctuation (activation) mechanism of elementary acts doesn't take place.

The cases of experimental observation of low-temperature plateau for velocities of these reactions are noted in wide consideration of kinetics of solid-phase chemical reactions and it is shown that such plateau is connected with quantum nature, in particular, with tunneling of reaction elementary acts [6]. The rupture of stressed interatomic bonds is the one type of the chemical reactions in solid (reaction of destruction or dissociation).

The obtained data on "temperature plateau" for durability of investigated polymer compositions can have important mean as they show the possible change of failure mechanism of elementary acts at transition from moderate temperatures to low ones.



a)



b)

Fig.3. The rupture tension of SC samples of PP-PELD: a) temperature dependences at $\sigma = 75$ MPa (1), 90 (2) and 100 MPa (3); b) force dependence for low temperature interval.

The structure change of loaded samples due to plastic deformation of metals or polymer orientation exhaust leads to change of durability because of local condition changes of load action [1]. The deformability increase with temperature increasing for the polymer compositions can influence on the samples of polymer compositions and because of that the oriented structure appearance. It leads to composition hardening and durability increasing. Consequently, the singular compensation of thermo-fluctuation decrease of durability and increase of durability because of orientation takes place. The "plateau" similarity would take place but not only because of the change of failure mechanism.

The measurement of sample deformation (tension) from the application moment up to the rupture one is carried out for the purpose of the revealing of this question. It turns out that the sample rapid tension (fraction of a second) at application of constant load takes place in low temperature interval and further, the sample deformation in time remains practically constant up to its rupture. The level of this tension is proportional to load but it doesn't change with temperature in low temperature interval (fig.3).

The increase of sample elongation before the rupture with temperature is observed only at elevated temperatures. Thus, the observation of deformation low-temperature "plateau" (especially in this interval where "plateau" on durability is observed) allows us to consider that change of sample orientation state doesn't take place in low temperature interval.

Consequently the conclusion on the fact, that the athermal failure kinetics of investigated samples from polymer compositions takes place at low temperatures, has the additional experimental substantiations.

Thus, there is a conception to suppose that failure kinetics of given polymer compositions is controlled by tunneling processes in low temperature interval. The two types of tunneling processes leading to failure of polymer compositions can be given:

1) The tunneling ruptures of stressed polymer compositional molecules (atom chains) where the skeleton atom itself tunnels from the bound state through the dissociation barrier strongly increased by tension stress. Especially such process and its probability is considered in [7,8]. Note that such process is possible on principle and is enough obvious one at big tensile loads, i.e. the average waiting time can be accessible in laboratory conditions. The molecule ruptures at such transition mechanism from thermo-fluctuation (over-barrier) transition to tunneling (subbarrier) one take place

at temperatures consisting in the definite part from the Debye temperature and depending on tension stress [8]. The tunneling of massive particles (atoms) occurs and tunneling kinetics of intrinsic failure of polymer compositions (accumulation of molecule tunneling ruptures) takes place in this processes. The data in fig.2 (a) and (b) corresponds to given change of molecule rupture mechanism as transition temperature on thermosensitive one to athermal kinetics regularly decreases with stress increasing as it follows from [8]. At the same time it is seen from fig.2 (a) and (b) that temperature intervals of these transitions for different samples of polymer compositions differ insignificantly, i.e. influence of PMC on these transitions is practically weak that gives the foundation for consideration of other tunneling process.

2) The preparation of stressed molecules to the rupture due to tunneling electron ionization.

There are experimental data showing the participation of electron processes in mechanical failure of polymers and their compositions. Thus, the acceleration of polymer mechanical failure and their compositions investigated in present paper at application of electrostatic field [9] is observed. The electron emission at polymer tension [10] is also revealed.

That's why one can give the following explanation of failure mechanism of polymer compositions in athermal region. As it is known if the polymer molecule ionizes so the rupture density of molecule section near the place of electron departure strongly decreases [11]. If we suppose that the electron tunneling output from skeleton atom in trap neighboring with molecule (inter-chain cavities) for strongly stressed macro-molecule becomes possible, then such ionized molecule will be rapidly failed. At such mechanism the rupture waiting time is controlled by the waiting of tunneling ionization act. The consideration of tunneling electron output from stressed polymer molecules at fluctuation local molecule tensions is given in [12].

CONCLUSION

The experimental observation of low-temperature plateau for mechanical durability of polymer compositions PP-PELD and also the supposition about possibility of tunneling process participation in failure kinetics and statement of question on concrete forms of these tunneling processes are the main conclusions of present paper.

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