Mechanisms of change of superficial properties of polymeric materials in discharge plasma

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Abstract. In work analytical expressions for assessment of the tribochemical changes and definition of the most effective direction of regulation of contact interactions are received. These results can be used for the analysis of experimental data at a research of mechanisms of change of polymeric materials superficial properties.

1. Introduction

In practice for improvement of physical and chemical properties of materials of the electronic equipment, the creation of the set superficial nanostructures by etching and thermal annealing, the ion-beam and thermal methods of activation and modification of materials are widely used [1–6]. At the same time the offered recommendations, technical solutions in this area have empirical character as systematic researches of the nature of the proceeding processes, their influences, for example, on morphology, the adsorptive, electrophysical properties of materials are practically absent. Under certain conditions of such activation the manifestation of specific radiation and stimulated physical and chemical processes which are capable essential to change structure of polymeric materials and their operational properties [4, 7-8].

2. Technique of calculations

Within the relaxation and diffusive theory of interphase processes [9] the opportunity of the analytical description of the processes proceeding in the radiation modified polymeric materials when using various schemes of their processing is given. At the same time the main attention is paid to consideration of influence of a dose of radiation and processing time on kinetics of adhesive interaction, value of friction force, wear intensity of materials at operation in friction couple.

At activation (electromagnetic or corpuscular) impact on materials [3, 7] in superficial layers of polymers the following main processes proceed: – heating, activation of diffusive processes; – excitation and ionization of macromolecules; – a rupture of macromolecules, formation of low-molecular fragments, free radicals and ions, the subsequent processes of interaction with their participation; – the subsequent chemical transformations of active fragments, ions and radicals, their interaction among themselves and with atoms of the contacting environment (stitching, oxidation, etc. processes); – dispersion (etching) of the modified superficial layer under the influence of ions, high-
vigorous particles, activation influence; – structural and morphological changes as a result of decrease of molecular weight, increase of segmental mobility, polarity of macromolecules etc.

As a result after processing depending on the nature of polymer, a dose of radiation and temperature formation of polar groups, for example, –OH, –O–C–, =N–O–, is possible, low-molecular products of thermal degradation, radiolysis, which are localized on the surface of material and interact with molecular fragments, exerting corresponding impact on their superficial properties [1].

In the relaxation-diffusive theory superficial properties of material are determined by value of density of the active centers (AC), their distribution by layer thickness. Generation of the active centers, the nature of their influence on processes of adhesive interaction depend on conditions of carrying out activation processing. At the same time realization of two main characteristic of technological receptions is possible: carrying out preliminary activation processing of material; a combination of ionic activation influence with other processes, for example, sedimentation of covering, at adhesive interaction, friction, etc.

At assessment of efficiency of preliminary modifying of polymeric material it is necessary to consider the nature of the proceeding post-radiation processes which kinetics is defined by concentration and stability of the formed active particles (radicals, ions, etc.), temperature and the oxidizing environment.

When carrying out activation processing of a surface the external environment can play a role of chemically active element of system and in it as a result of influence factors (ions, electrons, electromagnetic radiation) the corresponding processes influencing their properties also proceed.

In [10, 11] it is shown that superficial properties of polymeric materials enough with difficulty depend from nature substances, intensity of influence, and also temperature. Increase of the adsorptive activity of a surface at rather low doses of activation processing is connected with emergence in superficial layers of the acyl and peroxide radicals and their subsequent oxidation. The polar groups which are on a surface carry out a role of the active centers and increase adhesion interaction. In some cases change of properties in the course of processing is explained also with generation of the low-molecular products which are formed in polymer at influence of radiation, ions, their subsequent ion- or thermostimulated desorption.

Taking into account the representations stated above when determining energy of interphases interaction E at adhesive contact with other surface corresponds to expression [9]:

\[ E = N_0 \varphi(t) \bar{u}(t) + \int_0^t v_\varphi(t) \varphi(t-\tau) \bar{u}(t-\tau) d\tau, \] (1)

where \( N_0 \) – density of the communications which are formed on a surface in a contact zone in initial moment; \( v_\varphi(t) \) - speed of generation of adhesive communications in the course of contact; \( \varphi(t-\tau) \) и \( \bar{u}(t-\tau) \) – the functions describing change of density of adhesive communications and their average energy in the course of interaction respectively.

It is necessary to consider a number of the physical and chemical processes proceeding in superficial layers of the radiation-modified materials:

– radiation and the ion-stimulating destruction of macromolecules. In this case changes of AC can be defined by a ratio:

\[ dN_\varphi = n_0 (\alpha_1 q_1 + \alpha_2 q_2) dt, \] (2)

where: \( n_0 \) – density of macromolecules in superficial layer; \( q_1, q_2 \) – power of the radiation and ionic components of the activating stream; \( \alpha_1, \alpha_2 \) – the coefficients defining resistance of macromolecules to destruction at impact of radiation and a stream of ions respectively;

– change of the chemical composition of macromolecules as a result of interaction with active molecules of the environment as oxidation;

\[ dN_c = k_C dt, \] (3)

where: \( C \) – concentration of reactive atoms of the environment;
– etching of in superficial layer by high-vigorous corpuscular stream.

The kinetics of ionic dispersion will register: 

$$dN_{mp} = -k_2 N q_2 dt,$$

where \( k_2 \) – etching coefficient (ionic dispersion).

Density of the active centers of macromolecules \( N \), its change in processing influences the size of density of adhesive communications \( N_p \). In case of contact of polymer with the surface of other material having the sum of the areas of active microsites of \( S_a \) on the planimetric surface of contact by square \( S_0 \), according to [4]:

$$dN_a = a W dN_p,$$

The surfaces of substrate fixed on the active centers of macromolecules don't participate in further processes of generation of adhesive communications therefore change of number of the free active centers \( N \) of macromolecules on a surface taking into account ratios (2), (3) is described by the relaxation equation:

$$\frac{dN}{dt} = \frac{N_0 - N}{\tau_p} + n_0 (\alpha_1 q_1 + \alpha_2 q_2) + k_1 C - k_2 N q_2,$$

where: \( N_0 \) – number of the active centers which are in superficial layer and capable to come on a surface; \( \tau_p \) – characteristic time of diffusion relaxation of the active centers.

The solution of the equation (6) under an entry condition \( N(t=0)=N_1 \) is expression:

$$N = \left( N_1 - \frac{c}{b} \right) \exp(-bt) + \frac{c}{b},$$

where \( c = \frac{N_0}{\tau_p} + n_0 (\alpha_1 q_1 + \alpha_2 q_2) + k_1 C ; \quad b = \frac{1}{\tau_p} + k_2 q_2 \).

On the basis of (5) taking into account (7) we will receive expression for density of adhesive communications \( N_a \) in the form:

$$N_a = \frac{S_0}{S_0} \left( C - N_0 \right) \left[ \left( N_1 - \frac{c}{b} \right) \frac{1}{(-2b)} \left( \exp(-2bt) - 1 \right) - \frac{c}{b^2} (e^{-bt} - 1) \right],$$

At initial stage in processing \( t \ll 1/b \) density of the active centers linearly increases under the law \( N = N_1 + N_{st} (bt-1) \), where \( N_{st} \) – the stationary density of AC.

The analysis (7) shows that quasistationary value of density of AC is defined by the power of active processing and a ratio of its electromagnetic and ionic components.

$$N_{st} = \frac{N_0 + n_0 (\alpha_1 q_1 + \alpha_2 q_2) \tau_p + \tau_p k_1 C}{1 + k_2 q_2 \tau_p}.$$

At ion-beam activation it is possible to accept that \( q_1 = 0 \) and if mobility of AC is very low \((1/\tau_p \) is close to 0) and there is no change of the chemical composition of a polymer superficial layer \((k_1 = 0)\) stationary value of density of AC is equal:

$$N_{st, u} = n_0 \frac{\alpha_2}{k_2}.$$

At such processing the activation effect which is shown in change of number of AC doesn't depend on power and dose of ionic processing. Here change of parameters of adhesive interaction is reached only by etching of surface.

When processing in the smoldering category of plasma for which it is characteristic the combination of impact on the processed surface of the accelerated ions and UF-radiations, size of concentration \( N_{st, u} \) AC will be equal:
\[ N_{st,sl} = \frac{n_0}{k_2} \left( \alpha_1 \frac{q_1}{q_2} + \alpha_2 \right), \quad (11) \]

At comparable values of parameters of ion-plasma processing of a surface of polymeric material change of concentration of AC is defined as:

\[ \Delta N = N_{st,sl} - N_{st,lu} = \frac{n_0}{k_2} \alpha_1 \frac{q_1}{q_2}, \quad (12) \]

Thus, on the basis of (12) it is possible to conclude that processing in the smoldering category is more effective, and the maximum activation influence is reached in the presence in a stream, influencing a surface, of intensive electromagnetic radiation. Let's note that the parameters \( k_1, k_2, \alpha_1, \alpha_2 \) in the ratios given above depend from nature of polymeric material, temperatures and their values substantially define activation effect.

3. Conclusions
The received analytical expressions for special cases give the chance to estimate extent of influence on superficial processes of these or that radiation or the tribochemical changes, to define the most effective directions of regulation of contact interactions, and also to use them for the analysis of experimental data. So, the analysis of ratios (7), (9) – (11) allows to note features of kinetics of the adsorptive influence, the most effective methods of decrease of parameters of contact interaction, for example, as a result of decrease of segmental mobility of macromolecules, generation of low-molecular products.

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