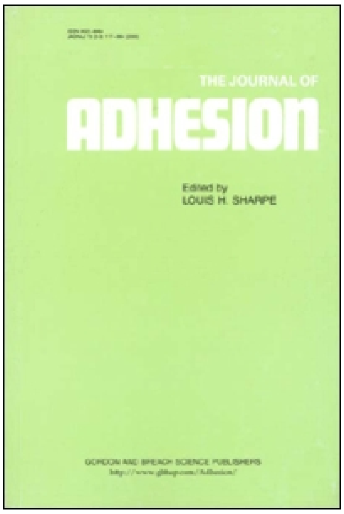

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N. A. Krotova[a]; N. N. Stefanovich[a]; A. I. Vilensky[a]; Ju. A. Chrustalev[a]
[a] Institute of Physical Chemistry, U.S.S.R. Academy of Sciences, Moscow, U.S.S.R.

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Investigation of the Electroadhesion Properties of Modified Polymer Surfaces†

N. A. KROTOVA, N. N. STEFANOVICH, A. I. VILENSKY,
and Ju. A. CHRUSTALEV

*Institute of Physical Chemistry, U.S.S.R. Academy of Sciences,
Moscow, U.S.S.R.*

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The effect of modification of the PTFE film surface on its adhesion and on mechanoelectron emission has been studied. If previously treated in glow discharge, PTFE gains significant adhesion strength up to the value 200 kg. per sq. sm. The increase of the adhesion strength is due to free peroxy radicals of the activated PTFE surface. The disjunction of the contact (treated PETF-polyepoxide) gives rise to emission with electron energies of 40 kev and initial intensity of 10^4 imp/sec. It becomes possible to vary the electroadhesion properties of treated surfaces through reactions of free peroxy radicals of activated surface with diverse reagents. The adhesion strength and emission intensity depend on the nature of functional groups on the surface. There is a correlation between the adhesion strength and emission intensity for different modified surfaces. These results are in a good agreement with the electronic theory of adhesion, the strength of adhesive joint depending on the charge density of the electric double layer, produced by collective donor-acceptor interactions at the interface. The acceleration of electrons in high electric fields in gaps formed on breakdown of adhesion contact accounts for phenomena of high energy electron emission in vacuum. Intensity of the post-emission from *freshly-formed* breakdown surfaces is a function of time. Mechanoemission is considered to be a type of autoelectron emission, caused by the residual charge field of freshly formed surface.

The electrostatic interactions at the interface between two components of an adhesion pair play the fundamental role in adhesion phenomena. The theory of such interactions was developed by B. V. Derjaguin and V. P. Smilga[1]. In the case of adhesion of two polymers the electron density redistribution in

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the contact area due to the interactions of the interfacial discrete donor-acceptor pairs was shown to result in the formation of an electric double layer. The following equation is valid for the latter:

$$\frac{n}{N_d} = \frac{1}{1 + \exp -\dfrac{(W_0 + \gamma n)}{kT}}, \tag{1}$$

where N_d is the concentration of donors,

n—the number of donor-acceptor pairs,

w_0—the energy of interactions, which is in general a function of n, k—the Boltzmann constant, T—absolute temperature.

$$\gamma = 4\pi \mathrm{e}^2 b \left(\frac{d_1}{\varepsilon_1} + \frac{d_2}{\varepsilon_2}\right), \tag{2}$$

where b = const ≈ 1, e – the electron charge,

d_1 and d_2 are the distances between the interface and the minimum of the potential pit, for the electron in donor and acceptor centers, respectively, ε_1 and ε_2 are the dielectric constants of the contacting phases.

The value of n is determined graphically by solving the transcendent Eq. (1). N_d can be obtained experimentally, the values of d_1 and d_2 are given, w_0 is constant in the first approximation. Using the obtained value of n one can estimate the charge density $\sigma = ne$ (3) and calculate the adhesion force $F = 2\pi\sigma^2$ (4).

The present paper is devoted to an experimental verification of these theoretical predictions. The carriers of the adhesion properties of polymers are functional groups playing the role of donors and acceptors in an adhesion contact. Let us assume one of the contacting surfaces to be saturated with donors and the other one with acceptors, the partners being placed opposite or "almost opposite" to each other. The equilibrium state of the system is determined from the free energy minimum condition which is a function of the number of reacting donor–acceptor pairs. The experimental verification of the theory can be performed for the systems whose surface is modified by specified functional groups. In our previous runs we observed the dependence of the electric double layer density and that of the adhesion properties, on the chemical modification of the surface[2]. The minor or even zero adhesion was observed if the electric double layer was not formed. The work of adhesion and the double layer charge density were found to change concurrently and in a similar way if the surface were saturated with donor and acceptor groups.

The variations in adhesion properties of polytetrafluoroethylene (PTFE) surface treated in a glow discharge (GD) and further modified by grafting of vinyl polymers with different functional groups were investigated. The value of adhesion strength of "epoxy-modified PTFE" bonding depends on the nature of the grafted functional group and increases in the order polystyrene < polymethylmethacrylate < acrylic acid < polyvinylacetate < polyvinyl alcohol < GD activated PTFE[3]. The latter is of particular interest, stable free peroxy radicals being generated at the activated surface. Their total concentration is about 10^{14} radicals per cm^2.[4] It is due to the radicals of the activated PTFE surface that the adhesion strength increases. In the case of adhesion contact between GD treated PTFE film and hydroxyl containing adhesives the formation of hydrogen bonds takes place, the $ROO^\cdot$ and —OH groups being acceptors and donors, respectively. The character of this hydrogen bond is electrostatic[5].

Formation of the bond at the interface, followed by an electron density redistribution in the contact region, must result in the formation of the electric double layer.

This fact is confirmed by the generation of an intense and long-term electron emission from polymer surface upon the failure of the "GD treated PTFE-polyepoxy" adhesion contact (Figure 1). The energies of electrons

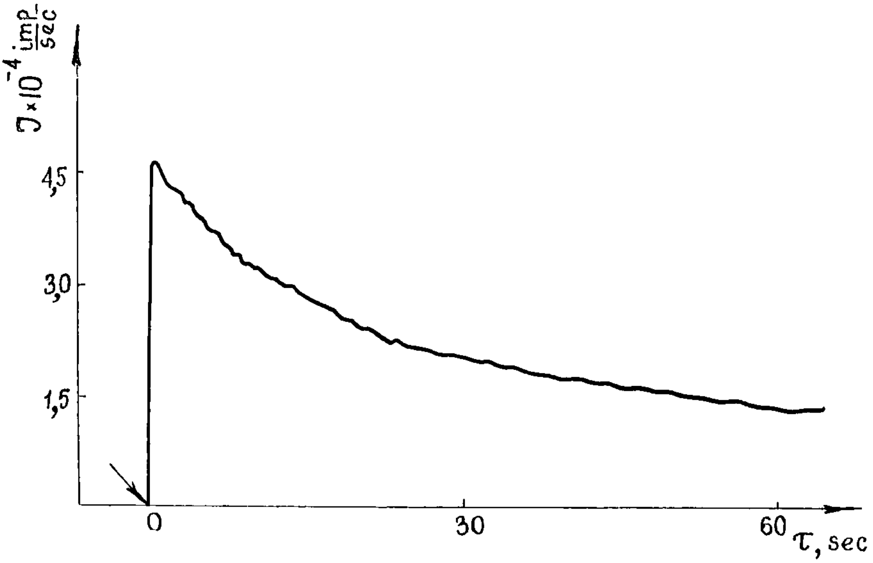

FIGURE 1 The postemission record on failure of "GD treated PTFE—polyepoxy" adhesion contact.

are estimated from the Al foil piercing and they reach 40 kev. The emission of electrons passing through the foil at the energies exceeding 40 kev falls down very sharply. The electroadhesion properties not only of ROO$^{\cdot}$ containing PTFE surfaces but of those saturated with ROOH, ONO_2 and —C=O groups were investigated.

In order to obtain an ROOH-containing surface a GD treated PTFE surface saturated with free radicals was submerged in the hydroquinone solution in alcohol. This caused the detachment of a hydrogen atom from a hydroquinone molecule and formation of hydroperoxide—ROOH. To obtain an ONO_2-saturated surface an activated PTFE film was treated with nitrogen oxide. The surface with —C=O groups was prepared by heating of a PTFE film, activated in GD, up to 200°C. The formation of —C=O groups is a result of radical recombination. The formation of all these groups on the PTFE surface was controlled by IR-spectroscopy.

Table 1 represents the data on adhesion of modified surfaces to epoxy in juxtaposition with the intensity of emission arising upon the break of adhesion contact. The emission intensity is seen to correlate with the value of adhesion for diverse modified surfaces. Besides the initial peak of emission produced by stripping, a more or less long-term post-emission was observed.

TABLE I

The emission intensity upon the failure of the adhesion contact and the adhesion strength of the modified surfaces

Functional groups on the surface	Emission intensity I, impacts per sec.	Adhesion strength kg. per cm^2
ROO$^{\cdot}$	4.7×10^4	160–180
ROOH	2.0×10^4	170
$RONO_2$	4.3×10^3	112
RO	4.0×10^3	80

The post-emission from the PTFE surface containing ROO$^{\cdot}$ does not disappear even after a 6 hours interval, while the surface saturated with –ROOH groups emits only during 30 minutes.

The post-emission of the newly formed surfaces was caused by the residual surface charge. It can be shown that the following expression is valid for the emission-time history:

$$I = I_0(1 + \tau^{-k}) \qquad (5)$$

where τ is the time.

I_0—the constant which characterizes the initial emission intensity,

K—the constant characterizing the rate of the emission relaxation, which depends on the electroconductivity of the system. The Eq. (5) is derived theoretically, the mechanoemission being viewed as a sort of autoelectron emission due to the field of residual charge on a freshly formed surface[6]. An example of post-emission relaxation on logarithmic scale is presented in Figure 2.

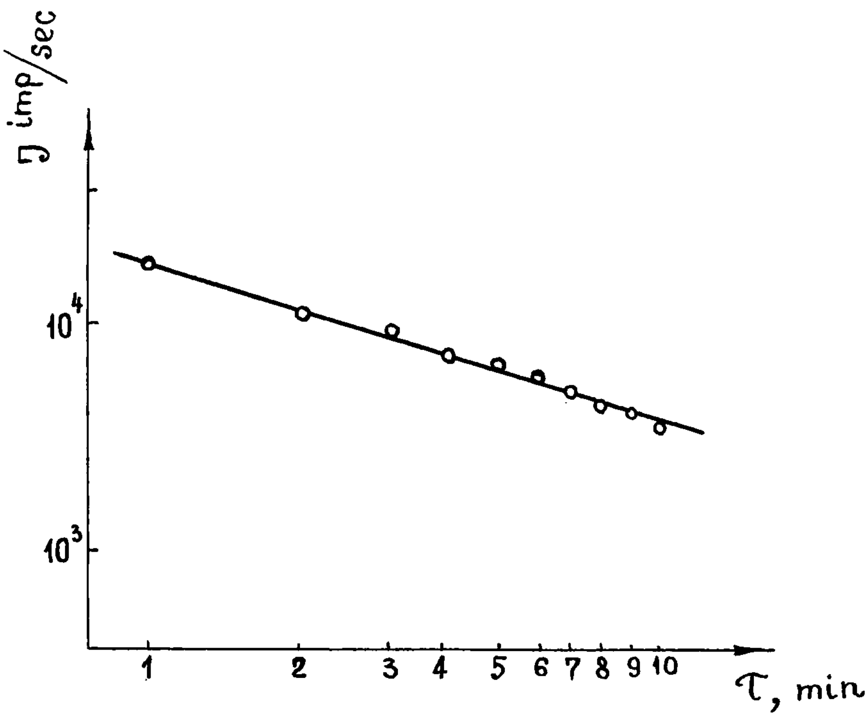

FIGURE 2 The fall of postemission from the modified PTFE surface (on logarithmic scale)

As stated above the adhesion of polymers is due to the donor-acceptor interactions in the contact area. Using the Eq. (1) and the diagram of Figure 3, one can calculate through the experimental data the number n of the donor-acceptor pairs involved in reaction. If N_d is 10^{14} radials per cm^2, n is 10^{13}. The charge density of the double layer and the specific adhesion is calculated using the Eqs. (3) and (4), respectively. σ can be estimated also from the energies of electrons emitting on stripping. Both values may be juxtaposed. Table 2 demonstrates a reasonable agreement between the experimental and theoretical values of adhesion and those of double layer charge density, the latter being determined by two different methods: 1) through the calculations with the use of the Derjaguin–Smilga equation, 2) through the data on the energies of mechanoelectrons.

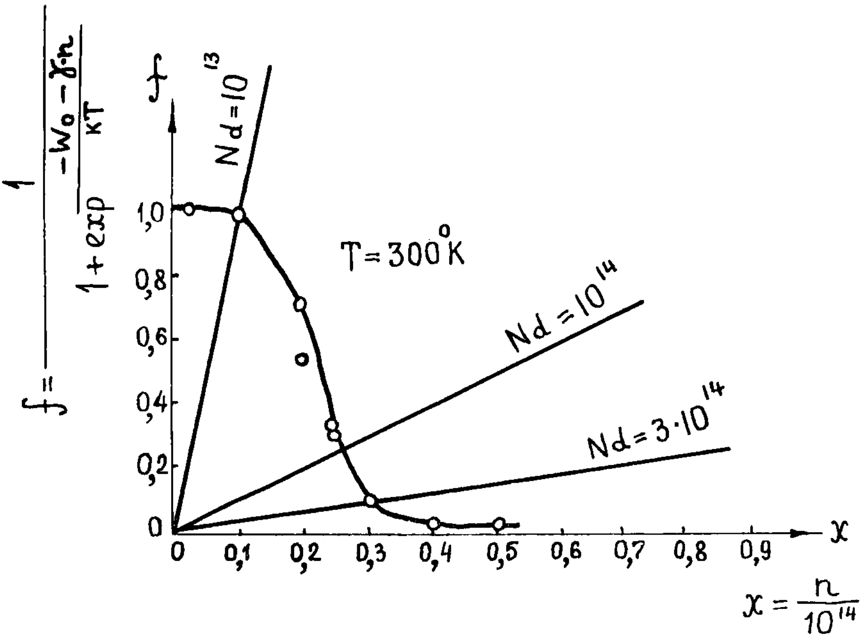

FIGURE 3 The graph for the calculating of the amount of donor-acceptor pairs reacting on adhesion contact.

TABLE II

Comparison of theoretical values of adhesion and double layer charge density with experimental ones

	Calculated values	Experimental values
F, kg. per cm^2	150	160–180
σ, CGSE	1) 4.8×10^3	—
	2) 4.6×10^3	—

Thus all the principal regularities of the electroadhesion phenomena in polymers can be followed for the modified PTFE surfaces: 1) The formation of the electric double layer at the boundary between two contacting polymers, 2) Emission of high energy electrons upon the failure of the adhesion contact, which testifies the presence of the double layer, 3) The post-emission phenomena due to the field of residual charge, 4) The sensitivity of the adhesion properties to the variations in the nature and in the concentration of the functional groups on the surface, 5) The close interrelation between the variations in the number of the functional groups (stable free radicals), the chemical activity of the surface and its adhesion ability,

6) The role of the donor-acceptor interactions in this process, the integral effect being connected with an unsymmetrical distribution of the electron density in the contact area.

All this together with good agreement between the experimental and theoretical values of adhesion and coincidence of the values of electric double layer charge density calculated by two methods, represents a convincing evidence on the decisive role of the electrostatic component in adhesion. In fact, there is no contradiction between the conceptions of the role of chemical and electrostatic forces in the adhesion phenomena.

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