THE RELATIVE ROLE OF ELECTRICAL AND DIFFUSION PROCESSES IN THE PHENOMENA OF ADHESION OF TWO POLYMERS

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Abstract

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THE RELATIVE ROLE OF ELECTRICAL AND DIFFUSION PROCESSES IN THE PHENOMENA OF ADHESION OF TWO POLYMERS

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In previous works by one of us ([1]), concepts of the electrical theory of adhesion were developed. On the other hand, various authors have repeatedly expressed views concerning the role of diffusion processes in the formation of adhesive and autohesive bonds ([2]).

Because the question is debatable, experimental study of the formation of an adhesive bond is of special importance, in particular when joining two high-molecular materials, in order to elucidate the relative role of electrical and diffusion processes in adhesion phenomena.

For resolving the question of the nature of the adhesive bond, the form of the adhesiogram is highly indicative. The influence of the rate of separation is comparatively small when the adhesive bond is due to diffusion phenomena. If, however, the adhesive bond is electrical in nature, the adhesiogram usually reveals three clearly expressed regions ([3]).

Table 1

Work of separation A_0 of polymer films from various surfaces and the velocity of electrons emitted in the process of separation at $P = 10^{-4}$ mm Hg.*

Polymer	Substrate	Electron velocity, eV	A_0 exper., erg/cm^2	A, calc. from electron velocity, erg/cm^2
Perchlorovinyl	Brass	$2.45 \cdot 10^8$	$2.45 \cdot 10^4$	$1.04 \cdot 10^4$
Perchlorovinyl	Glass	$6.25 \cdot 10^3$	$3.16 \cdot 10^4$	$2.52 \cdot 10^4$
Perchlorovinyl	Gelatin	$1 \cdot 10^4$	$3.16 \cdot 10^5$	$2.82 \cdot 10^5$
Perchlorovinyl	SKB rubber (filled with kaolin)	$2.5 \cdot 10^4$	$1.59 \cdot 10^6$	$5.63 \cdot 10^5$

Figure 1

Figure 1: Figure 1

Polymer	Substrate	Electron velocity, eV	A_0 exper., erg/cm^2	A, calc. from electron velocity, erg/cm^2
Polyisobutylene	Gelatin	$1 \cdot 10^4$	$3.56 \cdot 10^5$	$3.17 \cdot 10^5$

* The experiment was carried out in vacuum; the curve was taken in the region of high rates.

By means of a roller adhesiometer we obtained adhesiograms for a number of polymers (BF-type adhesive, polyurethanes, polyamides, vinyl-series polymers, rubbers and gutta-percha, cellulose esters, etc.). Adhesiograms of different combinations of these polymers with glass, metal, and rubbers based on Na-butadiene rubber and nitrile rubber usually give three clearly expressed regions. However, in some cases there are only two regions, and the third is absent. It is very likely that it nevertheless exists, but is located in the region of considerable rates, experimental determination of which becomes difficult.*

The velocity of the electrons emitted during separation ([4]) can give us an idea of the magnitude of the potential gradient of the double electric layer, since the electrons are accelerated by the fields existing in the gap between the surfaces being separated. By determining the velocities of the emitted electrons from the magnitude of the deflection of the electron beam in a magnetic field, one can—

* Under the conditions of our experiment, time intervals < 0.01 sec could not be measured.

but, having calculated σ from the experimental data and Paschen' s curve, one may calculate the work of separation $\overline{A}$ and compare this quantity with the value A_0 determined experimentally by a mechanical method (Table 1). It follows from the table that the higher the velocity of the emitted electrons, the greater the adhesion of the system.

In one of our recent works (5) it was established that, in the polymer film after separation, there are emission centers, and that separate regions of the film emit —

Fig. 1. Emission from regions of a film (1) of perchlorovinyl that were bound to the mechanically treated surface of a metal (brass), i.e., to deep grooves in the metal

—namely those regions of the film that had had the closest contact with the substrate. It is generally known that mechanical treatment of the substrate

Figure 3

Figure 2: Figure 3

surface leads to an increase in adhesive strength, which is usually explained by an increase in the contact surface area.* Therefore it was of definite interest to us to investigate whether the emission intensity of the separated polymer film would indeed be increased in those regions where it had been in contact with a mechanically treated surface. For this purpose, grooves were made with a file on the surface of the metal (brass), after which a polymer solution was applied to this surface. The experiment was carried out on a vacuum roller adhesiometer. In the photographs it is clearly visible that in the regions of the polymer film that separated from the grooves in the metal, the electron emission is most intense (Fig. 1).

Fig. 3. Electron emission from the surface of rubbers when a gutta-percha film is separated from them. *a*—rubber with kaolin filler, —rubber with carbon-black filler

Experience shows that the systems we studied are divided into two large groups (Table 2). The first group is characterized by electrical phenomena upon disruption of the adhesive bond: luminescence in medium vacuum, electron emission in high vacuum, and the presence of residual charge on the separated surfaces. The sign of the charge was determined by means of a simple radiometric circuit, and in all cases there was observed—

* However, this phenomenon may also be explained by other causes, for example, by a change in the surface properties of mechanically treated surfaces or by thinning of the oxide film.

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Fig. 4. Dislocations and stresses in a corundum crystal. The specimen is cut along the basal plane. 52×.
a—revealing dislocations by the method of selective etching; the vertical row of figures is a block boundary, the remaining rows are slip lines;
b—the same specimen in crossed polaroids; the slip lines are bordered by stress bands.

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Fig. 2. Microphotograph of transverse sections of systems:
a—perchlorovinyl (1)—SKN rubber (2);
b—gutta-percha (1)—paraffin (2). 100×

Table 2

Various types of adhesive bond

Nature of the adhesive bond	Sign of the residual charge upon separation in air	Emits upon separation in vacuum at $P = 1 \cdot 10^{-4}$ mm Hg	Work of separation at $v = 1$ cm/sec*	Type of separation
I group.Electrostatic interaction of charges of the double electric layer formed on the separation surfaces	Perchlorovinyl (−) –steel (+)Perchlorovinyl (−) –glass (+)	Perchlorovinyl	$1.04 \cdot 10^4 2.52 \cdot 10^4$	Adhesive”
	Polyethylene (−) –SKB rubber (+) (kaolin)**	Polyethylene	$4.45 \cdot 10^4$	”
	Polyethylene (−) –SKN rubber (+) (kaolin)	”	$5.63 \cdot 10^4$	”
	Gutta-percha (−) –glass (+)	Gutta-percha	$1.78 \cdot 10^5$	”
	Polyvinyl butyral (−) –SKB rubber (+) (kaolin)	Polyvinyl butyral	$2.02 \cdot 10^5$	”
	Perchlorovinyl (−) –gelatin (+)	Perchlorovinyl	$2.82 \cdot 10^5$	”
	Polyamide (−) –SKB rubber (+) (kaolin)	Polyamide	$3.01 \cdot 10^5$	”
	Nitrocellulose (−) –SKB rubber (+) (kaolin)	Nitrocellulose	$3.16 \cdot 10^5$	”
	Gutta-percha (−) –steel (+)	Gutta-percha	$3.98 \cdot 10^5$	”

Nature of the adhesive bond	Sign of the residual charge upon separation in air	Emits upon separation in vacuum at $P = 1 \cdot 10^{-4}$ mm Hg	Work of separation at $v = 1$ cm/sec*	Type of separation
	BF-6 (−) – SKB rubber (+) (kaolin filler)	BF-6	$3.98 \cdot 10^5$	”
	Perchlorovinyl (−) –SKB rubber (+) (kaolin)	Perchlorovinyl	$5.63 \cdot 10^5$	”
	Polyurethane (−) –SKB rubber (+) (kaolin)	Polyurethane	$6.32 \cdot 10^5$	”
	Gutta-percha (−) –SKB rubber (soot), treated with H_2SO_4 (+)	Gutta-percha	$6.52 \cdot 10^5$	”
	Gutta-percha (−) –SKN rubber (+) (kaolin)	”	$1.05 \cdot 10^6$	”
	Polyamide (−) –SKN rubber (+) (kaolin)	Polyamide	$1.12 \cdot 10^6$	”
a. Role of electrical phenomena not clarified	Polyethylene (−) –SKB rubber (+) (soot)	No emission	$4.45 \cdot 10^4$	”
	Polyvinyl butyral (−) –SKB rubber (+) (soot)	””	$1.75 \cdot 10^5$	”
	Polyamide (−) –SKB rubber (+) (soot)	””	$2.84 \cdot 10^5$	”

Nature of the adhesive bond	Sign of the residual charge upon separation in air	Emits upon separation in vacuum at $P = 1 \cdot 10^{-4}$ mm Hg	Work of separation at $v = 1$ cm/sec*	Type of separation
	Nitrocellulose (−) –SKB rubber (+) (soot)	""	$3.04 \cdot 10^5$	"
	Perchlorovinyl (−) –SKB rubber (+) (soot)	""	$5.41 \cdot 10^5$	"
	BF-6 (−) – SKB rubber (+) (soot)	""	$3.87 \cdot 10^5$	"
	Polyurethane (−) –SKB rubber (+) (soot)	""	$6.23 \cdot 10^5$	"
b. Adhesion > cohesion	No charge:Nitrocellulose –SKN rubber (kaolin)	""	$3.0 \cdot 10^6$	Cohesive(the rubber delaminates)
	Perchlorovinyl –SKN rubber (kaolin)	""	$3.0 \cdot 10^6$	The same
	Polyurethane –SKN rubber (kaolin)	""	$3.0 \cdot 10^6$	"
	BF-6 –SKN rubber (kaolin)	""	$3.0 \cdot 10^6$	"
	Perchlorovinyl –SKB rubber (soot), treated with H_2SO_4	""	$3.0 \cdot 10^6$	"

Nature of the adhesive bond	Sign of the residual charge upon separation in air	Emits upon separation in vacuum at $P = 1 \cdot 10^{-4}$ mm Hg	Work of separation at $v = 1$ cm/sec*	Type of separation
II groupFormation of an adhesive bond by diffusion of segments of polymer chains	No charge:Polyethylene —polyisobutylene	""	$1.19 \cdot 10^6$	Mixed
	Polyethylene —paraffin	""	$5.04 \cdot 10^5$	"
	Gutta-percha —paraffin	""	$5.04 \cdot 10^5$	"

* This rate usually corresponds to the region in which electrical phenomena are observed in systems of group I.
** Kaolin and soot were used as fillers.

the following regularity: the surface emitting electrons upon separation had a negative sign of the residual charge; the surface opposite to it, which did not exhibit emission, carried a residual charge of positive sign. Examination of microscopic sections (Fig. 2a and b) shows the presence of a clear interface between two polymers of this group. In some cases, with especially high adhesion, delamination occurs through the polymer film. In this case neither electron emission nor residual charge is detected on the separated surfaces. The work of separation is very high; moreover, evidently the work of adhesion is greater than the work of cohesion. Such systems are formed from components possessing strong polar groups (for example, BF-6 and rubber based on nitrile rubber, perchlorovinyl and rubber whose surface has been treated with concentrated H_2SO_4 and then washed).

Experience shows that the nature of the rubber filler plays a major role. If one of the components is rubber based on SKB with a carbon-black filler, no electron emission is observed when a polymer film is detached from it*, although the separated surfaces exhibit residual charges of opposite sign. When the polymer is detached from the same rubber, but with a kaolin filler, very intense electron emission is observed (Fig. 3).

Fig. 4. Effect of treating the surface of rubber (SKB) with acid and alkali of various concentrations on the adhesion of perchlorovinyl to it.

Substantial differences are presented by the systems of the second group (Fig.

Fig. 4. Effect of treating the surface of rubber (SKB) with acid and alkali of various concentrations on the adhesion of perchlorovinyl to it.

Figure 3: Fig. 4. Effect of treating the surface of rubber (SKB) with acid and alkali of various concentrations on the adhesion of perchlorovinyl to it.

2b), formed from nonpolar components. When the components of these systems are separated, no electron emission is observed and there is no charge on the separated surfaces. Microscopic examination of sections reveals a blurred interface. It must be acknowledged that, in systems of the second group, the adhesive bond is formed by diffusion of the polymer chains in the contact zone.

The reaction of the substrate plays a major role in adhesion phenomena, as is shown by our studies of the adhesion of perchlorovinyl to SKB rubber. It follows from Fig. 4 that the maximum adhesion A_0 corresponds to rubber treated with $1\,N$ H_2SO_4.

Residual charge is observed on the separated surfaces: negative on the polymer film and positive on the rubber.

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Note: Figure translations are in progress. See original paper for figures.