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Boundary Layers and Physico-Mechanical Properties of Adhesive Joints: Part I Experimental Background

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Various hypotheses of boundary layer formation in adhesive joints are reviewed. The features of boundary layers in joints obtained by means of thermoplastic and thermoreactive adhesives are studied, and substrate boundary layers are estimated. The examples of influence of density, elasticity modulus and other properties of boundary layers upon adhesive joint properties are presented.

An original method to design adhesive joints is proposed, based on the concept of special boundary layer properties. By means of this method the problem of mechanical performance of an adhesive lap shear joint is solved. The effects of various parameters of the theoretical model are compared with the experimental data.

KEY WORDS Adhesive joints, boundary layers, adhesives, physical-mechanical properties, joint design, stresses, deformations, strength.

1. IDEA OF BOUNDARY LAYERS

It is known that polymer (adhesive) properties in adhesives joint can differ from the polymer properties in the unconstraint state or, as it is usually said, in bulk. Since polymer in adhesive joint is in the form of a thin layer, it is expected, that

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polymer properties, measured in the form of thin films, will be equal to the properties of the same polymer in adhesive joint. This hypothesis attributes all possible property differences between polymers in adhesive joint and polymers in bulky specimens, to the geometrical differences between three dimensional, bulk specimens and film specimens in which one of the dimensions is very small in comparison with the others.

According to the second hypothesis, the cause of the property difference of the bulk polymer and polymer in adhesive joints lies in the interaction (chemical and or physical) between polymer and substrate.

The first hypothesis allows us in some cases to use in analyses direct comparisons of film and bulk specimen properties. The second hypothesis requires a more detailed consideration and formulation of new working hypotheses concerning with possible interactions between adhesive and substrate. This led to notion of a boundary layer defining the adhesive layer adjacent to substrate surface. The properties of this thin layer could differ from the polymer properties of the adhesive in the rest of the adhesive film.

For a long time, physical and chemical investigations have been conducted separately,^{1,2} each considering specific interaction mechanism of macromolecules with solid-state surface.

The chemical hypothesis assumes that the interaction between macromolecules and solid surface, can lead to formation of chemical and physical bonds. The forming of these bonds is preceded by adsorption of the macromolecules on the surface. In this process the selective adsorption of polymer components on the active surface centers should be considered. The course of these processes is affected by the activation energies associated with the transformations taking place at the polymer-solid surface. This process, which is limited in time because polymer segment mobility vanishes on hardening, leads to composition and property change of the polymer boundary layer.

According to physical-chemical hypothesis, the change of polymer structure near solid surface can be caused by steric effects, reduced mobility of macromolecules and their segments because of the orienting influence of solid surface. This reduces the conformations of macromolecule and changes the polymer structure and properties at and near the boundary layer.

Another boundary layer hypothesis considers the presence of defects associated with initial contamination of solid surface and by the presence of impurities, which in the process of polymer hardening migrate or are forced to migrate, to the adhesive-substrate boundary.³ The first part of this hypothesis (migration) is clear. However, for the second (forced migration) part, there is no good idea about the underlying mechanism such as pressing out of the impurities (e.g. plasticizers) caused by a pressure gradient. The problem is that there is no clear reason and mechanism of the existence of a pressure gradient.

In addition to these hypotheses, two others—thermophysical and deformative⁴—were proposed later. The nature of thermophysical hypothesis comes back to the difference in thermal conditions of polymerization (hardening) in thin layers and in bulk. As the polymerization process usually is exothermic, thermal conditions in bulk are close to adiabatic conditions and those in thin polymer layers are close

to isothermic conditions. Therefore, polymer structure and properties in bulk can differ from those in boundary layers.

The effectiveness and development of this hypothesis is closely connected with the development of investigations and notions about temperature effects upon structure and property changes during hardening.

The deformation hypothesis focusses on deformation processes in the polymer boundary layer caused by hardening and cooling of the adhesive joint. This hypothesis encompasses the effects of glueing and coating, the effects of specimen shape, etc. Thus, for example, the boundary layer on the flat surface is usually under tension. This results from the fact that the layer is formed and the adhesive interaction takes place when polymer is in a mobile state. Then, in the process of polymer hardening, the adhesive interaction prevents or reduces the possible shrinkages. Therefore, the boundary layer is in tension and/or compressed, depending on the sign of dimensional changes. For example, if the solid base is closed (e.g. spherical), then chemically or physically induced dimensional changes, prevented by the base can result both in more dense and less dense boundary layers. This does not depend only on the sign of dimensional changes but also on the thickness of the polymer layer and the preparation of the adhesive joints.

While the deformation hypothesis is confirmed by experimental investigations,⁴⁻⁶ the technological one is so far limited to theoretical predictions.⁶ The hydrodynamic hypothesis can be based on a kinetic model to form a microheterogeneous polymer structure body,⁷ invoking the Avrami concept multicenter hardening-crystallization. These notions plus new data concerning interactions of solid bodies flowing in a viscous medium between each other and with the wall⁸ lead to the hydrodynamic hypothesis.

The change of polymer structure and properties in boundary layer can result from a combined action of the mechanism discussed previously or from a dominant process mechanism.

There should be no doubt about the existence of boundary layers in adhesive joints. The observations by means of optical and electron microscopy, ellipsometry, and a number of mechanical methods indicate the existence of boundary layers.

However, a calculation method to determine the stress-strain state of adhesive joints, which includes the boundary layer concept, requires the understanding of the boundary layer formation.

Chemical, physico-chemical and thermophysical hypotheses take into consideration the substrate roughness and defects in the layer. Therefore, realistic boundary layer models must include a physical layer with special properties.

However, according to the deformation hypothesis, the boundary layer is the consequence of stress-strained state of system. These residual stresses should also be accounted for, which would improve the solution but further complicate the problems.

To obtain a realistic estimate of the boundary layer characteristics it is, therefore, necessary to employ investigation methods, that would allow us to determine the relative contribution of the previously mentioned mechanism of boundary layer formation.

Parallel to these investigations, it is also necessary to work out direct methods

allowing us to estimate the mechanical and geometrical parameters of boundary layer such as elasticity modulus and thickness.

At present, the boundary layer characteristics are estimated using an indirect method involving a combination of calculations and experimental methods.^{2,6,9}

For example, the calculation of some "integral" characteristic of composites based on its components' properties (matrix and filler), is carried out according to a certain model, without taking into account the boundary layer. The measurement of this characteristic is then determined by experiment. The deviation of estimated performance from experimental test data is then attributed to the boundary layer. Using a three-component model analysis (that is, taking into account the boundary layer), the properties and volume fraction of boundary layer are defined. It is obvious that the accuracy and even validity of such estimation depend on the accuracy of the initial composite model. For example, for the calculation of elastic characteristics of a filled polymer, in which the filler particles are randomly distributed in the matrix, the models assuming an ordered distribution are usually used. However, as the experimental investigations show, the models assuming regular structures are sometimes unable to predict the correct values for the elastic characteristics of such composites, and also fail to show the correct qualitative changes of these characteristics, as function of the filler content, etc. The models assuming a random distribution of filler particles on the other hand, predict the occurrence of percolation effects. These models predict larger increases of elasticity modulus with increasing filler content because of formation of continuous clusters consisting of filler particles.¹⁰

It follows from the previous discussion that the comparison of the properties of adhesives in the adhesive joints and properties of bulk polymers is a very complex problem. We have no way of telling how large they can be and what effects the magnitude of this difference. Therefore, it is first necessary to study polymer properties in bulk and then proceed with the analysis of some basic properties to develop a "yardstick" for further comparisons of bulk properties and polymer properties in adhesive joint.

2. THE ORIGIN OF BOUNDARY LAYERS

The boundary layers differ in structure and chemical composition from the rest of the adhesive film. Therefore, they influence the physical and mechanical properties of adhesive joints. As noted previously the boundary layers can be affected by numerous material and processing factors. For example:

1. Thermoplastic adhesives may exhibit at the boundary, differences in the degree of crystallinity, crystallite dimensions and orientations, and other formation changes, caused by energetic and steric reasons. If the solutions of thermoplastics are used, even weak interaction between solvent and substrate during joint formation, can influence the structure of layers adjoining the substrate.

2. One-component thermosetting adhesives, such as phenol resins used without hardener, can form boundary layer, because of the selective adsorption of polymer segments or gel particles on the substrate, etc. The use of more common multi-

component thermosetting adhesives may involve for the same reason differences in hardener concentration at the boundary and the rest of the adhesive. This leads to changes in hardening degree and changes of boundary layer properties. Besides with the hardener, such composition differences can take place with plasticizing agents, solvents and other low molecular weight fluid components.

3. Various impurities in thermoplastic or in thermoreactive adhesives (such as unreacted components, contaminants, oxidation products etc.), can also migrate to the boundary during the formation of adhesive joint. This process becomes more important, if the impurities are incompatible with hardened adhesive.

4. Adhesive primers (finishing agents) applied onto the substrate, are by themselves boundary layers with specific mechanical properties. In addition, they change the degree of chemical or physico-chemical interaction between adhesive and substrate. This in turn influences the adhesive boundary layer. If the primers are added directly to the adhesive, they will also tend to concentrate at the boundary.

Let us now consider the substrate boundary layer effects of adhesive joints.

5. Substrate boundary layers, influencing the mechanical properties of adhesive joints, exist in many forms. With polymeric substrates, the boundary layers, may be created by molding, extrusion, pressing etc. They can differ from the bulk characteristics in structure, density, strength, surface properties etc. With ceramic, concrete and other mineral materials, the surface formed at the boundary with air, can differ from the bulk in the type and structure of crystal phase.

6. Metals may have oxide layers on the surface. Their mechanical properties, their bonds strength with metal and their surface characteristics influence significantly the mechanical properties of adhesive joints. This approach is widely used in practice. It is well known that formation of oxide layers on aluminium, titanium and other metals can significantly increase the strength and durability of adhesive joints.

7. The boundary layers, which form by surface impregnation of porous substrates with adhesive, are also important in practice. This is the case with some oxide layers of metals, many substrates of mineral nature (concrete, ceramics etc.), wood, wood products, paper etc.

For example, an adhesive flowing into the pores of an oxide layer leads to the formation of a specific impregnated layer. The mechanical characteristics of this layer can differ from the properties of both the initial oxide layer and of the adhesive boundary layer outside the pores. This is because the chemical and structural composition of pores can differ with pore site and geometry. This is the case with aluminium. In addition, the pore diameter affects the accessibility for various adhesive components which leads to segregation.

The role of impregnation process in formation of adhesive joints by glueing and painting is especially important with wood, wood products, paper etc.

Wood surface always contains cavities of out through cells, which are separated by cell walls. Since cell wall has a complicated structure and chemical composition, the interaction between adhesive and various areas of cut through cell wall will differ. However, in cell cavities adhesive gets into contact only with the primary cell wall, which consists mainly of hemicelluloses.

For most common relatively low density wood, the adhesive fraction in cell cavity

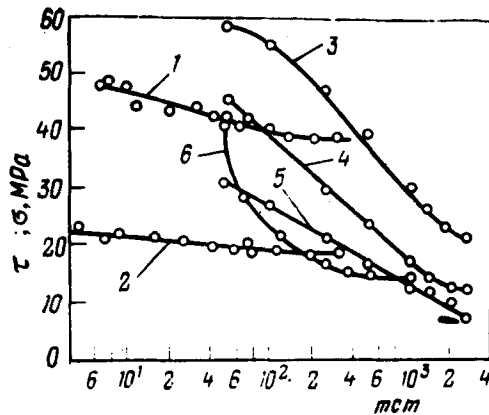


FIGURE 1 Relationship between glued joints and glue line thickness: 1, 2—torsional shear, epoxy adhesive K-115 (1—hardening 7 days and nights at 20°C; 2—7 days and nights at 20°C + 3 hours at 120°C); 3–5—uniform tension, epoxy adhesive E-40 (3—hardening 75 hours at 120°C, 4—75 hours at 20°C, 5—75 hours at 20°C adhesive with dibutylphthalate); 6—lap joint shear, phenol-rubber adhesive.

exceeds significantly the adhesive fraction in the intercellular space. REM and ESCA analyses show that phenol adhesive concentrates primarily in inner walls. Therefore, the strength of such joints is controlled by means of so called “rivet” effects resulting from the flow of adhesive into cavities.

The properties of impregnated boundary layer change significantly, if adhesive component influences actively the substrate and vice versa. The most characteristic example is destruction of wood surface layer by glueing with phenol adhesives of cold hardening type which use sulphonic acids as hardeners. In this case, the strength of adhesive joint often decreases on long service because of the acid hydrolysis of wood at the boundary between impregnated layer and bulk of wood.

The common difficulty is direct determination of physical and mechanical properties of boundary layers, regardless of their origin. The most density of boundary layers and the relationship between density and adhesive layer thickness are determined most frequently. The density changes frequently correlate with those of microhardness. The strength of very thin isolated adhesive layers is almost impossible to determine by means of standard mechanical methods. It is also difficult to quantitatively describe the adhesive joint with very thin adhesive layers, because the roughness height is usually comparable with that of boundary layer thickness. It must not be neglected that internal stress influences the relationship between the strength and glue line thickness. With the most uniform type of loading such as torsional shear this relationship is weak (Figure 1).^{11,12}

In torsional shear, the difference between the bulk mechanical properties of epoxy polymer (EDT-10) and those in adhesive joints are practically the same.

	Casting polymer tube	Adhesive steel joint
Fracture strength (torsion shear) MPa	55.2	56.8
Shear deformation, %	5.45	4.87
Young's modulus, MPa	1280	1360

This does not exclude the presence of boundary layers but it suggests, that any differences between the adhesive mechanical properties in the joint, and the bulk properties, should not be attributed to boundary layers.

It is comparatively easy to determine the dynamic modulus and mechanical losses of a substrate with thin coatings. Sometimes it is possible to isolate the substrate boundary impregnated with adhesive, and to measure its mechanical properties. This technique is practiced with wood, paper and similar materials.

The relaxation characteristics of the connected joint, undoubtedly correlate with strength and deformation of adhesive joints, are also affected by the boundary layer. The determination of glass transition temperature of thin polymer layers on a substrate are useful in explaining the temperature dependence of adhesive joints.

3. BOUNDARY LAYERS AND MECHANICAL PROPERTIES OF ADHESIVE JOINTS

Let us now consider some examples of the boundary layer effects on the characteristics of adhesive joints.

The substrate surface can influence the crystalline structure of boundary layers. A decrease in crystallinity on contact with metals reduces the inner stresses and increases strength and durability of adhesive systems.

In the systems metal foil-trifluoroethylene copolymer joint, the degree of crystallinity is reduced¹³ from 57 to 46%. In contact with copper, polyethylene, polyimide and nylon melts develop on cooling column structures in the boundary layer. However, on contact with aluminium hemispherulites are formed. Polymers with column structures exhibit higher deformability than those containing spherulites.¹⁴

The density difference between PMMA and polydimethylsiloxane near the surface of quartz and teflon, and in bulk is 3–5%. However, the boundary layer thickness on teflon is $2-4 \times 10^{-5}$ m and on quartz $30-40 \times 10^{-5}$ m.

The processing temperature effects the structure of crystalline polymers in adhesive joints. This is important in the manufacturing of metal-polymer joints. With an increase of mold surface temperature up to 80–110°C, the microhardness of polyamide coatings increases by 15–20 MPa, and strength of the polyamide-steel joint increases by 30–40%.¹⁵ When joints of polyethyleneterephthalate film with aluminium are quickly cooled in water, amorphous structure of polymer with lower density and internal stresses develops in the boundary layer. In this case, the joint strength is three times higher than that of joints cooled in air. In the latter case, the polymer has a crystalline structure, increased density, and exhibits high internal stresses.

In reinforced thermoplastics based on aramide fibers and aliphatic polyamide, in the layers with thickness of $0.5-1 \times 10^{-5}$ m, the crystallinity degree of polyamide decreases with increasing orientation along the fibers. At the same time, strength and rigidity of polyamide matrix increases up to levels which corresponds to properties at 300% tensile deformation.

The relationship between polyethylene microhardness and the distance from the

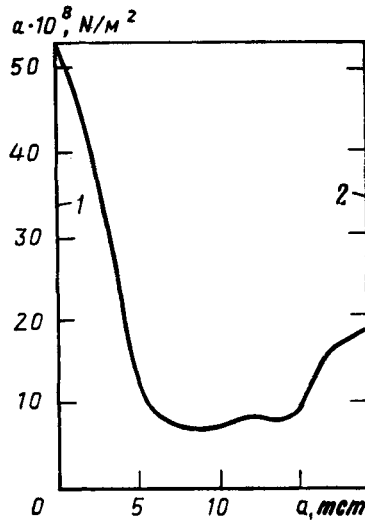


FIGURE 2 Microhardness profile a of polyethylene coating on silicon in thickness (1—free surface, 2—contact with silicon).

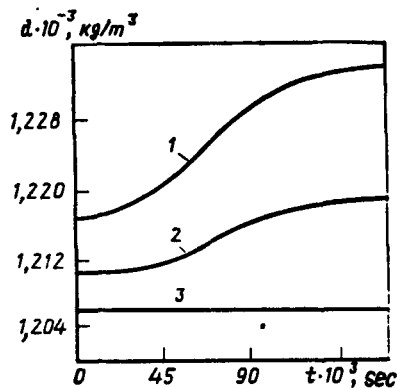


FIGURE 3 Relationship between density of polyepoxy films ($\text{Ed-20}^- + m\text{-phenylenediamine}$) with thickness ($R \times 10^{-4}$ m), as well as 0.7 (1), 2.0 (2) and 2.8 (3) on the treated glass and annealing time.

boundary polymer-substrate follow a complicated pattern (Figure 2), but the sensitivity to distance is highest at the boundary.¹⁶

The surface characteristics of the substrate influence also the structure of cross-linked polymers. Frequently, the effect reaches a depth of 200×10^{-5} m. The use of substrate with high surface energy promotes the formation of large size uniform domains of hardened phenol polymer, which improves the mechanical properties.

The increased boundary layer density of crosslinked polymers often leads to unbalanced performance. This is noted in volume relaxation caused by annealing of films removed from the substrate. The thinner is the film, the greater is the density increase on annealing (Figure 3).¹⁷ In this case, the cause of volume relaxation can be in residual stresses, that develop on adhesive joint formation. As a consequence of residual stress gradient along the normal to the substrate surface,

the inhomogeneity of adhesive structure appears. To obtain the boundary layer with minimum stresses, the hardening process should be carried out under such conditions, that the largest deformations associated with hardening take place, far from the gelation point.

With the reduction of coating film thickness, the segment mobility decreases. This is indicated by the position of the temperature of maximal mechanical losses. The removal of the upper layer of the coating changes¹⁸ the position of the maximum (Figure 4).

The effect of epoxy polymer coating thickness upon its modulus and glass transition temperature also depends on the substrate surface energy (Figure 5). In the case of low-energy surface, the glass transition temperature is rather insensitive to changes in coating thickness.¹⁹ With high energy surfaces, the boundary layer

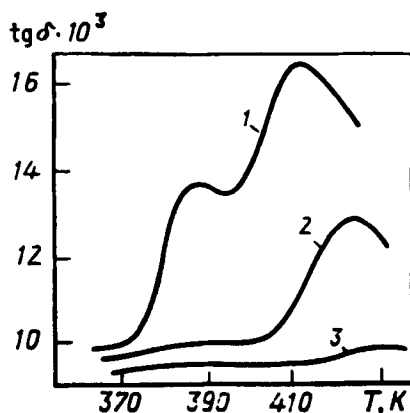


FIGURE 4 Relationship between the mechanical loss tangent due to temperature for initial epoxy coating with thickness 4×10^{-5} m (1) after removal of upper layer with thickness 2×10^{-5} m (2) and 3×10^{-5} m (3).

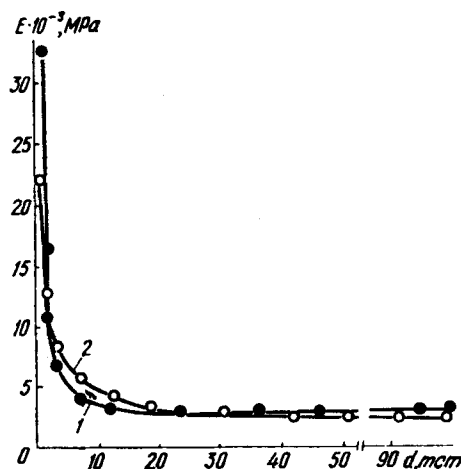


FIGURE 5 Relationship between Young's modulus of polyepoxide on quartz (1) as well as teflon (2) and coating thickness.

structure is complicated, and the layers with thickness of 0.01×10^{-6} – 0.003×10^{-6} m do not harden without heat-up. It has been reported, that depending on the type of epoxy resin and hardener, the hardening degree of composition at the boundary with quartz, glass, teflon, etc. (determined by density, elasticity modulus and coefficient of volumetric expansion) can increase or decrease.^{20–23} This correlates with changes in glass transition temperature.

Sometimes, the binder of one type can influence the mechanical properties in the opposite way. This has been observed with the elasticity modulus and coefficient of volumetric expansion of hardened epoxy resins as a function of quartz filler content. As the filler content increases and, therefore, the fraction of boundary layers increases, the magnitude of the opposite effect becomes more intense (Figure 6).²⁴

The introduction of some surfactants into adhesive leads to more complete hardening of the boundary layer. This is the case with epoxy resin with octiltrimethylammonium bromide (OTAB). However, the observed increase of adhesive strength

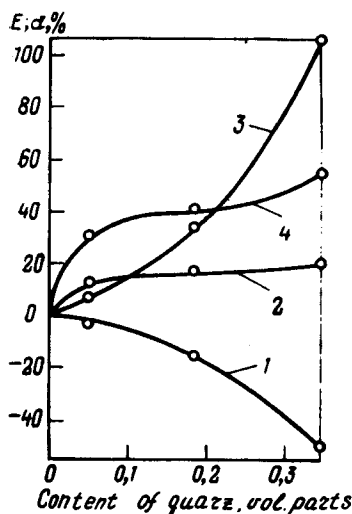


FIGURE 6 Relationship between relative values of Young's modulus E (1.3) and coefficient of thermal expansion up to T_g (2.4) of epoxy binders and volume contents of quartz binders on the base of aliphatic resin (1.2) and diphenylolpropane resin (3.4) hardened by m -phenylenediamine.

TABLE I

The influence of surfactant on adhesive strength and glass transition temperature of epoxy coatings

Concentration OTAB, %	Adhesive strength, MPa	T_g	
		Gas chromatography	Calorimetry
0	11	370	382
1	13	367	—
5	24	365	—
8	30	363	374
10	28	360	371
20	20	355	366

TABLE II

The influence of surfactant on Young's modulus $E \times 10^{-3}$ MPa of epoxy coatings on different substrates

Coatings thickness	Surfactant, %		
	0	5	10
	<i>Aluminum</i>		
1	27.0	34.0	16.0
2	10.0	14.5	6.8
5	5.0	5.5	3.5
10	4.3	4.7	2.4
20	3.2	2.9	2.2
	<i>Teflon</i>		
1	19.5	25.0	15.7
2	11.2	17.2	12.0
5	6.7	6.8	5.2
10	4.6	4.8	4.0
20	3.4	3.4	3.0

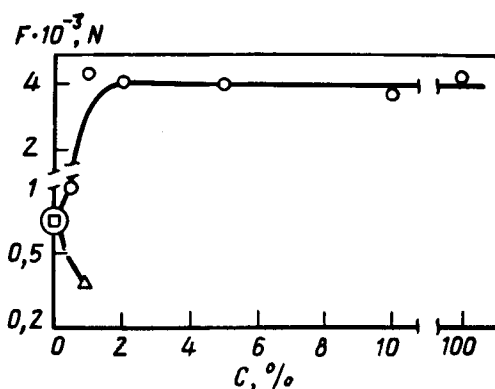


FIGURE 7 Relationship between adhesive interaction force F of the plane (111) of gold, as well as the plane (111) of copper (as well as copper alloys) and volume concentration of alloying element: \circ = alloy Cu—Al, \square = alloy Cu—Sn after ionic spraying; \triangle = alloy Cu—Sn after heating up to 200°C.

(Table I) may not be caused only by this effect, but could also originate in the plasticization processes. Note that with increasing OTAB content T_g decreases, but the strength increases. The surfactant effect is indirectly confirmed by the complicated relationship of elasticity modulus of epoxy coating at small coating thicknesses (Table II).

The influence of boundary layer is particularly noticeable when polymer or oligomer mixtures are used as adhesives. With compositions of epoxy or resorcinol resins and rubbers, a reduction in the dispersion phase (rubber) content is often noted at the boundary with metals. This leads to a reduction of impact resistance, crack resistance and other long term mechanical characteristics of adhesive joints.

The segregation of doping elements is observed in alloys, leading to differences between surface and volume concentration of elements. This can significantly change the adhesive strength. The introduction of 1% aluminum into copper increases

adhesion (Figure 7), while the ration between surface and volume concentration of these elements reaches a value of 6.5.

Regarding chemical processes in boundary layers, which influence the adhesive strength, polyethylene oxidation in joints with metals should be mentioned. Very strong effects of thermal treatment time and relationship between surface energy of the adhesive and delamination strength are shown in Table III. The final effect depends on the type of metal etc. For example, copper contributes intensely to polymer oxidation, but copper oxide is weakly connected with the bulk of metal. Therefore, the joint has low strength.

Regarding chemical processes in boundary layers, which lead to the increase of adhesive strength, the bromination of rubbers should be mentioned. Increases or decreases of fixed bromine in boundary layer, lead to parallel changes of adhesive joint strength.

The modification of substrate surface is very effective in increasing strength and durability of coatings, adhesive joints etc. Oxide layer on metals produced by different etching techniques can differ greatly in thickness and structure. For alu-

TABLE III

The influence of treatment polyethylene on boundary layer oxidation and adhesive strength

Treatment	Content of oxygen in boundary layer, %	Wetting angle	Shear strength, mH/m ²
Without treatment	0.25	98	0.55
Chromic acid etching (1 min, 20°C)	5.5	76	7.45
Contact oxidation (10 min, 150°C)	3.75	78	5.65
Gas-flame treatment (1.2 sec, air: gas = 4:1)	6.8	—	5.1

TABLE IV

The influence treatment by pickling process of polyolephines on their surface properties and adhesive strength

Treatment	Atomic ratio		Oxygen content in SO ₃ H, %	Wetting angle	Shear strength, MPa
	C:S	O:S			
<i>Polyethylene</i>					
Without treatment	—	—	—	98	0.55
1 min, 20°C	269	14.9	0.37	76	7.45
30 min, 70°C	80	12.2	1.25	66	7.58
6 h, 70°C	47.1	11.2	2.22	45	9.48
6 h, 70°C + 12 h H ₂ O	59.2	14.1	1.69	64	6.06
<i>Polypropylene</i>					
Without treatment	—	—	—	92	0.28
1 min, 20°C	283	19.1	0.35	73	4.69
1 min, 20°C + 12 h H ₂ O	583	27.1	0.19	82	4.83
6 h, 70°C	261	15.9	0.38	97	11.2

TABLE V

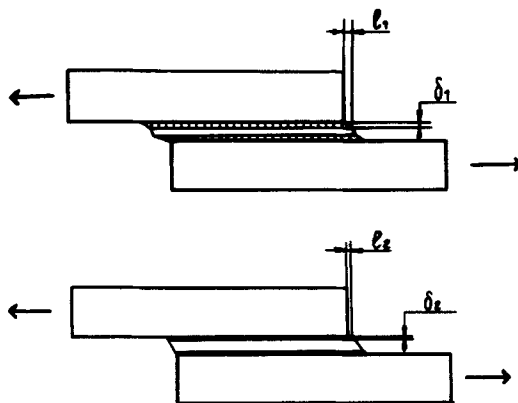
The influence of metals finishing on adhesive joint strength

Adhesive	Testing temperature, °C	Lap joint strength		
		Without finishing	1% γ -aminopropyl-triethoxysilane	1% γ -mercaptopropyl-trimethoxysilane
Nitril-phenolic	20	10.2	16.5	22.0
	180	1.3	3.0	18.0
	250	0.8	1.8	2.5
Butvar-phenolic	20	16.8	19.0	20.8
	80	12	2.9	5.1
	120	2.1	2.5	2.7
Epoxy	20	9.9	11.8	11.1
	80	7.9	12.7	13.2

TABLE VI

The influence of silane ES-1 finishing of metals on their shear joint strength (epoxy adhesive EPC-1)

Type of shear	Treatment	Strength, MPa	Variation coefficient, %
<i>Aluminum</i>			
Compression	without finish	30.2	9.25
	with finish	31.9	6.27
Tension (lap joint)	without finish	10.6	8.12
	with finish	12.9	6.75
<i>Steel</i>			
Torsion of rings	without finish	45.1	5.74
	with finish	43.9	5.69



$$\delta_1 > \delta_2$$

$$l_1 > l_2$$

FIGURE 8 Influence of boundary layer thickness (δ) on deformability (l) of adhesive joint.

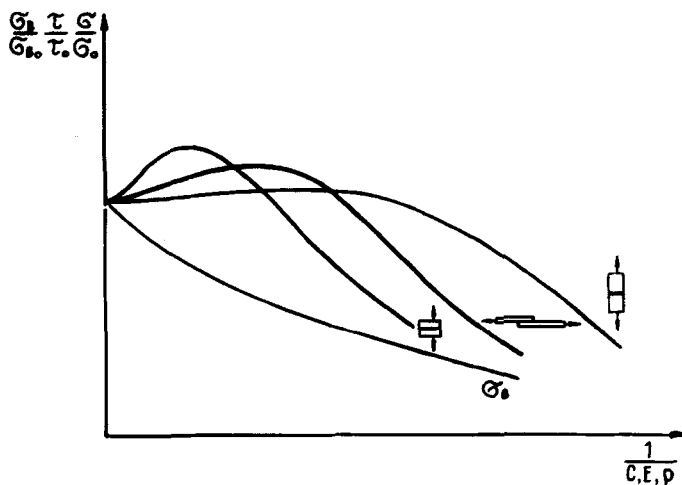


FIGURE 9 Relationship between adhesive joint strength by shear, by uniform tension and change, as well as by inner stresses and boundary layer properties.

minum alloys, porous structure of oxide layer is of great significance, and so is the reduction of magnesium content in the boundary layer by etching. At magnesium content of 8–10% in the form of $MgAlO_4$, the strength of joints with polyethylene is greatly reduced.²⁴

In addition, removal of magnesium increases the water resistance of joints. Strength and durability of adhesive joints is increased by treatment of aluminum alloys with phosphoric acid solutions. The phosphatization of steel before paint coatings is also widely used, because it produced large increases in adhesive strength. The anodizing of aluminum alloys, leads to increases in adhesive joint strength up to a certain thickness level of anodized film. Here, the adhesive fills the pores and creates a rivet effect.

Brassing of ferrous metals is widely used in rubber-metal joints. High strength is achieved by sulphur vulcanization of these pairs. Maximum adhesive strength is obtained at $Cu_{1.97}S$ ratio in the boundary layer. The thickness of such boundary layer is 30–50 nm.

With polyolefines, teflon and some other thermoplastics the strength of joints is increased by etching, treatment with corona discharge, plasma etc. The composition of corresponding boundary layers can vary significantly, and the changes of surface properties do not always correlate with the adhesive strength. This indicates existence of additional changes in the surface topology (Table IV).

Treatment of carbon fibers for composite materials significantly affects the adhesive strength. Oxidation with formation of active functional groups in boundary layer is the most effective. In this case, the shear strength of carbon reinforced plastics increases to the highest observed levels.

The substrate finishing raises only modestly the initial strength of joints (Table V) and depends on stressed state (Table VI), but its effect on water resistance is greatly improved.

Low-molecular finishing agents form very thin boundary layer and its deformation ability is rather low (Figure 8), therefore, reducing the possibility for stress

relaxation. Thicker polymer finishes have advantages in this respect. Thin layer finishes with relatively high ability of deformation could be very effective boundary layers for high strength but brittle adhesives. For example, the combination of phenol-rubber adhesive as a finish for a high heat resistant silicone adhesive is an example of such a pair.

In summary, the final effect of the boundary layers on adhesive joint performance depends on many factors acting simultaneously and in complicated relationships. This makes the forecasting of mechanical properties of adhesive pairs very difficult.

Nevertheless, we believe that common rules could be formulated, correlating the boundary layer characteristics with the physico-mechanical properties of adhesive joints. First, we assume, that most often the boundary layer differs in deformation properties from the rest of the adhesive. Next, we must conceive, whether the deformation ability caused by a change increases or decreases, and proceed from the stressed state of given joint (Figure 9). In this case one can deduce in which direction strength will change etc. The higher the stress concentration (both outer and internal), the greater will be the influence of boundary layer. However, the decreases in layer thickness reduce the effects of increased deformability, because the substrate walls hinder this process. In this regard, the boundary layers of polymer nature are more effective than low-molecular finishing agents.

The effect of water and other liquid media upon adhesive joints is particularly critical. The density reduction, lowering of hardening level etc., promote diffusion and penetrability.

Consequently, there are certain characteristics of boundary layers at which the physico-mechanical properties of a given adhesive joint and at a given type of loading and service conditions will be at optimum.

A method to determine the characteristics of boundary layers, which are necessary for mechanical design of adhesive joints, will be presented in the second part of this study.

SUMMARY AND CONCLUSIONS

1. Experimental evidence showing that bonding layers whose properties and structure are different from the rest of the adhesive layer has been presented.
2. Chemical and physical factors which affect the structure and properties of the boundary layer have been identified.
3. Significant effects of the boundary layer formation on the performance of adhesive joints have been identified and qualitatively interpreted.
4. The possibilities of a mathematical model has been envisioned that will enable us to predict the performance of adhesive joints and adjust their performance by controlling the boundary layer characteristics.

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