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New Ideas Concerning the Strength of Adhesive Joints of Polymers†

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The review was written by J.J.Bikerman specially for "Uspekhi Khimii". Bikerman is one of the leading U.S. specialists in the theory and practical aspects of surface phenomena and adhesion in polymers and solids and therefore the presentation of his views on the nature and strength of adhesive joints is of very considerable interest.
It is noteworthy that the views developed by the author depart widely from those common in the USSR and therefore his review is of special interest for the Soviet reader. Putting forward a number of interesting and well founded postulates of the rheological theory of adhesion, the author essentially ignores the molecular nature of adhesion phenomena, the chemical nature of adhesives as such, and the polymer nature of adhesives, which are not discussed in the review at all. Also ignored are the thermodynamic criteria of adhesion, the effects of the flexibility of the polymer chain and its structure on adhesion, etc. All these factors make the author's approach to adhesion somewhat one-sided and biased. However, this is compensated by a purposeful approach to the problem, a polemical presentation, and a number of postulates which are of very great practical value for all those concerned with adhesion and adhesive joints.
The bibliography includes 75 references.

CONTENTS

I.	Strength of adhints and molecular adhesion	651
II.	Hook-type adhints	652
III.	Improper adhints	653
IV.	Location of rupture	658
V.	Proper adhints	659
VI.	Dependence of strength on external and internal conditions	663

I. STRENGTH OF ADHINTS AND MOLECULAR ADHESION

In 1959 a valuable review on "Modern Views on the Adhesion of High Polymers" was published[1] in "Uspekhi Khimii". In the present paper an altogether different approach to the problem is employed. The author's views on the reason for the strength of adhesive joints (or adhints as they will be called henceforth for brevity) are described in the book which has been published in two editions[2]; readers who find this review too compressed and incomplete are referred to this monograph.

The mechanical rupture of an adhint requires the application of a stress f (g cm^{-1} s^{-2} or kg m^{-1} s^{-2}) or a force F (g cm s^{-1} or kgf m s^{-2}) and the performance of a certain amount of work W (g cm^2 s^{-1} of kg cm^2 s^{-2}). The problem of the factors which determine these quantities can be expressed also in a somewhat different form. Each adhesive joint contains several components; in the simple case there are two—the adhesive and the adherend—but there may be as many as five: the first adherend, the first boundary layer, the adhesive, the second boundary layer, and the second adherend. It is necessary to find a relation between the experimental values of f, F, or W on the one hand and the properties of these components and the geometry of the adhint on the other.

The second formulation of the problem may appear strange to unprepared readers and therefore it must be justified immediately. For many years everyone believed and even now it is still frequently believed that it is necessary to overcome *adhesion* in order to rupture an adhesive joint. Theoretical or molecular adhesion is by definition the attractive force A (per unit area) between the atoms or molecules of a substance A and the atoms and molecules of a substance B along the boundary between the phases A and B. It is assumed that the mechanics of rupture is fairly unimportant. If a stress f proves to be necessary in repeated experiments for the rupture of a joint between an adherend B and an adhesive A, the implication is, according to some theoreticians, that the adhesion A between A and B is equal to f. Thus one can obtain curves relating A to, for example, the chemical composition of A and B if the breaking stress f has been measured as a function of this composition. The geometry of the adhint and the mechanics of the experiment are disregarded, since the experimenter believes that he measures molecular adhesion, which is independent of external conditions such as the kind and direction of the breaking force, the form and size of the adhesive joint, etc.

In fact the resistance to rupture (f) is never and under no conditions equal to A. One can create fairly artificially an imaginary relation between f and A, as stated in section III, 1, but it is in all cases insignificant. The identification of f with A constitutes the apex of a pyramid made up of several strata of erroneous assumptions. The principal stratum or the principal error is the hypothesis that the theoretical adhesion A may be determined by mechanical measurements on adhints. The second unjustified hypothesis is that the force responsible for rupture is equal to the external force F applied to the adhesive joint. The third error consists in the fact that the macroscopic stress is assumed to be equal to the microscopic stress. The fourth stratum involves the assumption that the microscopic stress necessary to initiate rupture is equal to molecular adhesion.

The considerations set out in the previous paragraph may be elucidated using peeling as an example. In Fig. 1, A represents a rigid adherend, R a flexible ribbon, and G a layer of glue. A force F is applied to the free end of the ribbon. Evidently the force does not act directly on the edge E of the adhesive. Thus the first task of the investigator is to calculate or measure the force and moment acting on this edge and the crack formed in it; when the crack grows, the adhint gradually disintegrates.

† Edited by Yu.S. Lipatov.

The relation between the external force F and local stresses in the adhesive and at its boundary with air depends on the thickness and nature of the ribbon, on the thickness and nature of the layer of glue, etc; a mathematical expression for this relation is given in section V, 4. If the local stresses have been determined correctly, the second of the errors enumerated above is eliminated.

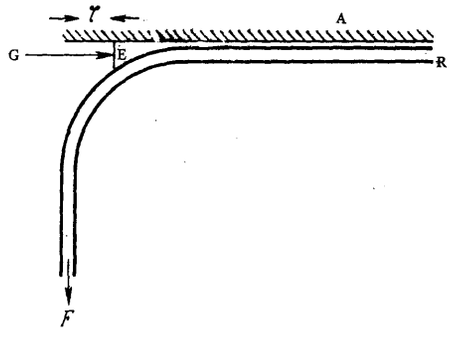


Figure 1. Peeling of a ribbon R from a rigid adherend A; G = adhesive; E = its edge.

All solids are inhomogeneous. They contain cavities, impurity inclusions, crystal lattice defects, and other flaws. Usually each flaw gives rise to a concentration of stresses in its vicinity. If the *average* stress along the cross-section of the solid is σ (g cm^{-1} s^{-2} or kgf m^{-1} s^{-2}), then the stress at the flaw may be 100 σ or even 1000 σ. The true *local* stress σ_m, which should be defined as "local at a square" [locally in a cross-section ?Ed. of Translation] is much greater than σ and a crack is initiated at the point where σ_m is particularly high. This is in fact, why for a given average stress σ, σ_m varies from point to point and solids disintegrate via a crack growth mechanism and not immediately into individual atoms or molecules. As long as the investigator bears firmly in mind the radical difference between σ and σ_m, he avoids the third error.

If the description of peeling described here is correct, then it is clear why one cannot employ the fourth stratum as a basis. The crack arises and spreads in the adhesive layer. In many systems its distance from the interface (adhesive — adherend) exceeds by a factor of hundreds and thousands the "radius of molecular action"; thus the phenomena which occur along the crack cannot depend on forces acting across its boundary.

Here one must ask the obvious question why cracks cannot originate and grow exactly between two solid phases. In this case one might expect the equality or at least a close relation between σ_m and A. The answer is that interfacial rupture is altogether unlikely. Fig. 2 illustrates the boundary between two solids; the circles represent the molecules of one solid and the crosses those of another. The [dotted] lines show that the crack spreading from left to right may be propagated in different ways. If the probabilities of all three ways are equal, the probability that the rupture will occur *between* the two phases is 1/3. The probability that the crack will occur between two phases at a distance equivalent to 11 molecules is $(\frac{1}{3})^{10}$, i.e. approximately 1 : 59 000; in other words an interfacial crack with a length equivalent to 11 molecules can be expected in only one adhint out of 59 000. The probability is even smaller if the attraction between the adhesive and the adherend (if the adherend is a material with strong cohesion) is mostly greater than the attraction between the molecules of the adhesive; this follows from the familiar general expression for van der Waals constants a: $a_{12} \simeq \sqrt{a_1 a_2}$, where a_1 is the constant for two molecules of type 1, a_2, the constant for two molecules of type 2, and a_{12} the constant for a molecule of type 1 and a molecule of type 2. If $a_1 > a_2$, then $a_{12} > a_2$. In a metal — adhesive — metal system, the numeral 1 refers to the metal and the numeral 2 to the adhesive.

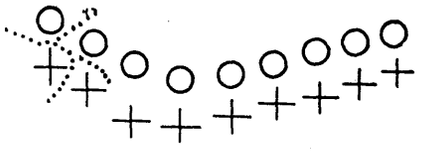


Figure 2. The growth of a crack (dotted lines) between two solid bodies.

The impossibility of rupture exactly along the interface can be proved also in a different way. Since the probability of finding a particularly weak spot in a solid is greater the larger the specimen, the breaking stress (and hence $\sigma_m : \sigma$) usually increases if the thickness of the plate undergoing rupture is reduced. The thickness of the adhesive layer is rarely below 0.01 cm and the "thickness of the slits" between different molecules in Fig. 2 may be estimated as 10^{-9} cm; evidently, for equal molecular forces, a smaller stress is needed to rupture a thicker layer.

Since material A cannot be separated from material B exactly along their boundary, the forces acting between A and B are not involved in the separation process; rupture takes place far from the boundary and the stress necessary for it cannot yield any information about the true adhesion between A and B. Thus the first postulate on which the upper part of the pyramid of errors rests is as misleading as the second. A more detailed examination of the problem of the value of A for the strength of adhints may be found in the author's book[2].

II. HOOK-TYPE ADHINTS

The main conclusion of the first section of this review is that the experimental values of f, F, and W are independent of the molecular adhesion A and cannot be used for its determination. The breaking stress is determined by the mechanical (and not chemical) properties of the components of the adhint and by the geometry of the system. The significance of this general rule can be more conveniently considered separately for each class of adhesive joint. From the standpoint of the mechanism of strength, there are three such classes. The simplest to understand and probably the oldest class is that of hook-type adhints, which occur in consequence of "mechanical adhesion". Their adherends are fibrous or porous solids (fabrics, paper, natural wood, etc.). During the formation of such joints, the liquid adhesive flows round the

fibres or filaments of the adherend and after solidification forms hook or loops around each fibre. When, say, a postage stamp is stuck to the envelope, the mechanism of joint formation differs little from the mechanism responsible for the joint between two fabrics sewn together. As in sewing, molecular contact between the adherend and the adhesive is not required in hook-type adhints, which constitutes an extremely favourable factor, since extensive purification of materials such as paper, cardboard, or wood is almost impossible even in the laboratory let alone in industry.

When a breaking force is applied to a hook-type adhint, one of the two components (the fibres of the adherend or the filaments of the adhesive) breaks because they cannot be separated in any other way; in certain systems the break occurs partly in one material and partly in the other. At any rate, f, F, and W are fully determined by the mechanical strength of the fibres which are intrinsically weak or at which the external force is concentrated; unfortunately a mathematical formulation of the strength of hook-type adhints does not as yet exist.

Generally speaking, in order to obtain satisfactory hook-type adhints, it is necessary to ensure that the adhesive penetrates the space between the adherend fibres and solidifies there. Thus the incorporation of the adhesive in the adherend is the most significant process in the life of a hook-type adhint. This process was investigated several years ago[3,4]. Two questions were investigated: (1) to what depth the adhesive should penetrate into the fibrous body in order that the strength of the adhint should reach its maximum possible value for the given system and (2) what time is necessary for such incorporation. Different types of paper and cardboard served as adherends and the extreme inhomogeneity of these materials has been the main source of the inaccuracy and the poor reproducibility of the quantitative results.

A clear answer to the first question was obtained for filter paper which is much more homogeneous than many other varieties. It was glued on one side to a thick metallic plate and on the other to an aluminium foil; the foil was peeled off after the solidification of the adhesive. For small amounts of glue (m, g m^{-2}), the resistance to peeling increased with m, but, when m exceeded 15 or 20, the resistance no longer depended on m. For this paper, 20 g per m^2 corresponded to a thickness of penetration to a depth of approximately 30 μm. The average diameter of the fibres in the paper was 8 — 10 μm. Thus it was sufficient to engage by the adhesive hooks two or three fibres in the bulk of the adherend in order to attain the maximum resistance possible for the given paper.

In these experiments the adhesive employed was a melt of poly(vinyl acetate). When an aqueous solution of dextrin was employed instead, the liquid penetrated into the adherend to a considerable depth, but left behind fewer hooks after the removal of solvent, so that peeling from paper glued with dextrin was easier for all values of m than when the melt was employed.

When the foil was stripped from a laminate cardboard, the results depended on whether the foil was glued to the edge or to the centre of the cardboard rectangle. In the first case the resistance was smaller, since the external force was transmitted immediately to the loosest of the layers and the crack passed along this layer. In the second case the cleavage had to begin in an external layer, which is usually denser and stronger than the others; therefore a much greater force was required to initiate peeling. As long as the experimentor believes that he is measuring molecular adhesion between the glue and the cardboard, it will not occur to him to alter the site of the joint from the edge to the centre and vice versa.

In order to answer this question, a polyethylene vessel containing a measured amount of glue was turned upside down with the opening pointing downwards towards the paper and was then drawn along the paper at a constant velocity (u, cm s^{-1}). The depth of penetration of the glue (τ, cm) was then measured with the aid of a microscope. If the diameter of the aperture is b (cm), each point on the surface of the paper remained in contact with the glue over a period b/u seconds. During this time, the glue penetrated into the adherend to a depth τ (cm), so that the average rate of penetration was $\tau u/b$ (cm s^{-1}). The measured values confirmed the simple hydrodynamic description of the process for simple liquids.

III. IMPROPER ADHINTS

The second class of adhesive joints is also of respectable antiquity but its nature was understood only several years ago. Improper joints contain weak boundary layers. The concept of weak boundary layers is as significant for the modern ("rheological") theory of adhesive joints as the rejection of the idea that rupture takes place exactly at the interface, as stated in the first section. The adherends in improper adhints either do not contain any pores and voids capable of being filled with glue or they have at least a dense surface layer: for example, paper coated with varnish or a dyed wooden plate may be incapable of being impregnated with glue; the usual metals, glasses, and plastics are also incapable of forming hook-type adhints. The absence of voids is a general property of adherends in improper and proper adhints.

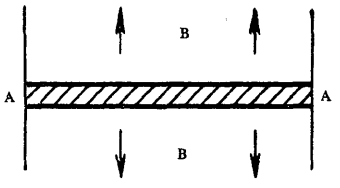


Figure 3. A proper butt joint. A = adhesive; B = adherends.

When it is said that two cylinders of a substance B are glued together with an adhesive A, only two materials are mentioned. In the schematic representation of such an adhint (Fig. 3) only two materials are indicated. In improper adhints there is at least one more substance, which is located on the boundary or along both boundaries between A and B (Fig. 4). When a breaking force is applied to the adhesive joint shown in Fig. 4, a crack arises in the boundary layer if its strength is less than that of the materials A and B. Thus the adhint is ruptured in the material which is not even mentioned in the description of the system and is determined by its properties.

According to their origin, weak boundary layers can be divided into seven groups, since three phases are involved in the formation of an adhesive joint: the medium (usually air), the adhesive, and the adherend. The material of

the weak layer can enter the adhint from the medium (air) (a), from the adhesive (b), from the adherend (c), from air and the adhesive (d), from air and the adherend (e), from the adhesive and the adherend (f) and from all three phases (g). Certain examples of these types will be described in the present section.

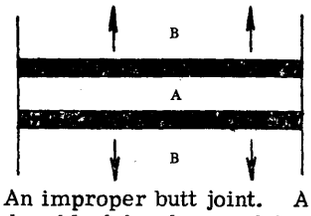


Figure 4. An improper butt joint. A = adhesive; B = adherends; black bands—weak boundary layers.

1. Weak boundary layers of the *first group* are frequently encountered. When the liquid adhesive spreads on the surface of the adherend, it must displace air from each hollow on the rough surface. If the displacement is incomplete, bubbles of air remain between the adherend and the solidified adhesive, as shown schematically in Fig. 5. Each bubble concentrates stresses in the adjoining regions of the solid; this effect was already mentioned in the first section and it is expressed by Eqn. (4) in the fifth section.

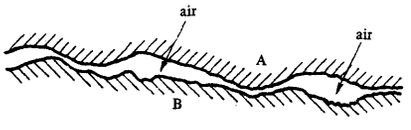


Figure 5. Air bubbles between an adherend B and an adhesive A which has not achieved complete contact with the adherend.

Air remains between the adhesive and the adherend either because the wetting of the adherend by the liquid adhesive is poor or because the adhesive joint was prepared hastily and sufficient time was not allowed for the liquid to flow into all the pits and grooves. Wetting is determined by the contact angle θ or more accurately the advancing contact angle θ_A. A modern treatment of contact angles was recently given in a book by the present author[5] but it is outside the scope of the present review. One need only point out that, when the equilibrium contact angle is zero and the advancing contact angle is negligibly small, one should employ as far as possible only adhesives giving $\theta = 0$ on the surface of the adherend.

One sometimes encounters the view that the requirement for $\theta = 0$ arises because the liquid wetting the solid has a strong affinity for it; it is believed that the liquid A displaces air from the surface of the adherend B because the molecular adhesion between A and B is high. This approach is unconvincing. The contact angle depends not only on the attraction of B to A but also on the attraction or air (or generally speaking a third phase) to A and to B. If, say, water wets poorly a solid surface, one cannot conclude that the attractive forces between these two phases are small; if the solid is heated in mercury until all the gases have volatilised and is then treated with water, the latter can readily displace mercury so that an impression will be created that the attraction of water to the adherend is high. One can appropriately mention here the mechanism of soldering. If a drop of liquid solder is deposited on what appears to be a metal the drop does not spread. Supporters of molecular adhesion have concluded that in this case the attraction between the metal and the solder is so weak that no adhesive joint is obtained. In reality liquid solvent does not displace air from the surface of the oxide but it does readily displace fused rosin from the surface of the metal.

An example resembling soldering was investigated by Nicholas and Poole[6]. Oxygen-free copper gave $\theta = 20°$ at 1200°C on tungsten and f for joints between tungsten and copper was approximately 1900 bars (1 bar = 10^6 g cm^{-1} s^{-2}). When there were 251 parts of oxygen per million parts of copper, θ reached 70° and f did not rise above 320 bars. A dark layer, the composition of which probably corresponded to the oxide WO_3, could be seen in this system as the boundary between copper and tungsten (a magnification of 450). The oxide did not behave itself as a weak boundary layer but copper did not wet it; this cavities remained between copper and the oxide after solidification.

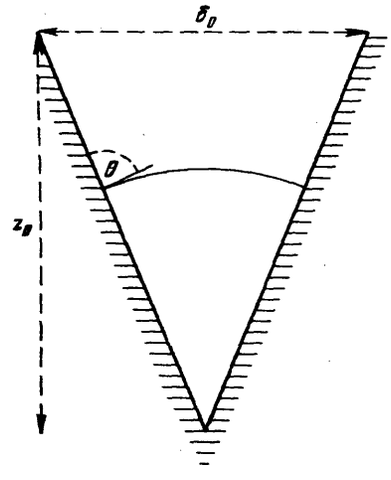


Figure 6. Displacement of air from a scratch by an adhesive flowing downwards. Maximum width of scratch—δ_0; depth—z_0; contact angle (in liquid adhesive)—θ.

In all probability the unwettability of polytetrafluoroethylene is the main reason why nothing can be glued to this polymer. There exists yet another possibility: namely that it contains impurities which act like those in polyethylene (see section III, 2), but it is difficult to reconcile this with the observation that PTFE copolymers fused and cooled on a clean metal surface (in air) form with the latter very strong adhesive joints.

The displacement of air by a liquid adhesive always requires some time and in many systems the time is very long. Hollows in solid surfaces usually have an irregular shape which is not susceptible to mathematical treatment. It is therefore necessary to resort to models. Fig. 6 shows a channel with a depth z_0 (cm) and a width at the top δ_0 (cm); a liquid fills it above and forms with the walls an advancing contact angle θ_A; the thin continuous lines indicate the position of the meniscus t seconds after the beginning of the experiment. The shortest distance between this line and the top of the channel is designated by the symbol z. If the surface tension and the viscosity of the liquid are denoted by the symbols γ (g s^{-1}) and η (g cm^{-1} s^{-1}) respectively, the following approximate formula is valid:

$$z_0 \ln \frac{z_0}{z_0 - z} - z = \frac{\delta_0 \gamma \cos \theta_A}{6\eta_m^{z_0}} t . \quad (1)$$

It is readily seen that z will equal z_0, i.e. the liquid will reach the bottom, only after an infinite time t whatever the values of γ and η. This result is obtained because the walls of the channel are assumed throughout to be ideally straight; since in reality they are rounded near the bottom, $z_0 - z$ reaches zero for finite values of t; at any rate, it is clear that haste in the preparation of adhints can result in the formation in the latter of weak boundary layers of the first group.

The flow of liquid may be accelerated by an external pressure[7], but this pressure P must be greater than the product $2\gamma\cos\theta_H/\delta_0$ (g cm^{-1} s^{-2}) in order to affect seriously the rate of flow; when θ_0 is small, i.e. the channel is a crack, the required P is much too high for practical purposes. The usual adhesives are non-Newtonian liquids, i.e. their viscosity depends on the rate of flow; estimates of this correction may be found in the literature[7,8]. The viscosity of the adhesive very often increases with the time it takes to fill the hollows in the adherend because of the evaporation of the solvent, the cooling of the melt, or a chemical reaction; if the rate of this increase is comparable to the rate of flow, the adhesive may solidify without reaching the bottom of the channel, so that air bubbles remain between the glue and the adherend[9].

2. Weak boundary layers of the *second group* consist of a substance which was previously contained in the adhesive. Industrial polyethylenes are the most thoroughly investigated representatives of this group. When the usual polyethylene is fused on a clean metal, glass, etc. support and is allowed to set, the solidified drop can be readily scraped off with a fingernail. Printing ink sticks to polyethylene but readily splits off from the latter on removal of the solvent. This lack of capacity of polyethylene for "adhesion" was previously explained, and even now continues to be explained[10], by the fact that the force field generated by the alkane chain $-CH_2-CH_2-CH_2-$ is weak; the attraction of methylene groups to solids is so weak that it can be readily overcome by a negligible external force.

The myth of the inadequate molecular adhesion of polyethylene was destroyed and the true cause of the weakness of polyethylene adhints was discovered in a series of investigations[11-15].

Firstly, technical polyethylene was purified by dissolution in boiling toluene or xylene and precipitation with acetone or butanone. The precipitate, which usually contained more than 95% of the initial polymer, did not contain polar groups (for example carbonyl groups) which can be almost always found by examining the infrared spectra of unpurified polyethylenes. The content of branched chains (for example isopropyl groups) was lower than in the initial material. Thus after purification the composition of polyethylene was closer than before to that of the ideal compound $-CH_2-CH_2-CH_2-$; nevertheless it proves to be an excellent adhesive and was used successfully to glue metals to metals, glasses to glasses, and glasses to metals[11]. All adhesive joints with purified polyethylene were made in an atmosphere of nitrogen in order to avoid oxidation.

In certain cases purification increased the tensile strength by a factor of 50. Such enormous increase of "adhesive capacity" could not be accounted for by a physical change in the material, since the density, wettability, and other measured properties did not alter appreciably as a result of purification. The author concluded that crude polyethylene contains impurities soluble in the liquid polymer and eliminated from it during solidification and crystallisation. Some of them accumulate in the surface layer. If they are almost liquid at the experimental temperature or their strength is reduced, the surface layer as a whole is characterised by a low resistance to rupture. Adhesive joints prepared with crude polyethylene must be represented by Fig. 4 and not Fig. 3; when a tearing axial force (arrows in Fig. 4) is applied, the weak boundary layer is split in two and the strength of this layer alone (and not of the polyethylene itself) determines the experimental strength of the adhint. Purified polyethylene contains almost no insoluble impurities, does not form weak boundary layers, and gives rise to strong adhesive joints.

Secondly, the resistance to rupture of the compounds just mentioned was compared[12] with the strength of polyethylene itself. If weak boundary layers are absent, the system consists of only two components: the adherend and the adhesive and rupture naturally occurs in the weaker phase. In all cases this was purified polyethylene, since the adherends were only metals (steel, copper, and aluminium) and glasses. Since the crack arose and spread in polyethylene, the rupture of the adherend — polyethylene — adherend system was largely analogous to the rupture of polyethylene itself. Fig. 7, which presents some of the results obtained by the present author and his coworkers[12,15], does indeed show that the strength of polyethylene adhesive butt joints is almost equal to the strength of polyethylene rods (the dashed line on the right-hand side of the diagram) when the layer of adhesive is fairly thick (for example 150 μm). The reason why the breaking stress f (expressed in bars in Fig. 8) increases when the thickness δ of the adhesive diminishes is explained in section V, 1. At any rate, it is clear that f is determined by the strength of the adhesive and has nothing in common with molecular adhesion between the adhesive and the adherend. Polyethylene could be seen with the naked eye or with the aid of the microscope on both rupture surfaces.

Thirdly, a low-molecular-weight substance was mixed with purified polyethylene in order to restore it to the "anti-adhesive" or non-glueing state[13]. Oleic acid, which is a typical polar compound, proved to be suitable for this purpose. On the basis of the molecular theory of adhesion, oleic acid should increase the "adhesive capacity" of non-polar polyethylene. In fact the admixture of 1 mg of the acid in 1 g of purified polyethylene reduced its resistance (Γ, g s^{-2}) to peeling (of aluminium foil glued with polyethylene to glass) and when the added concentration reached 1%, Γ fell to 10 kdyn cm^{-1} from 65 kdyn cm^{-1} for the uncontaminated polymer.

Fourthly the accumulation of oleic acid on the surface layer was confirmed by electrical measurements[14]. Purified polyethylene and its mixtures with 0.1, 0.2%, etc. of oleic acid were placed in an atmosphere of moist ammonia and the surface conductivity of the polymer was measured. The curve relating the surface conductivity $1/\chi$ to oleic acid concentration c was found to resemble very closely the $\Gamma = f(c)$ curve mentioned in the previous paragraph; when the concentration was raised from 0.1 to 0.4, $1/\chi$ fell by a factor of 6. Probably the limiting solubility of oleic acid in the solid polyethylene investigated is approximately 0.1%; when c is above this minimum, the excess acid accumulates near the surface, where it reacts with ammonia and forms ions responsible for the enhanced conductivity.

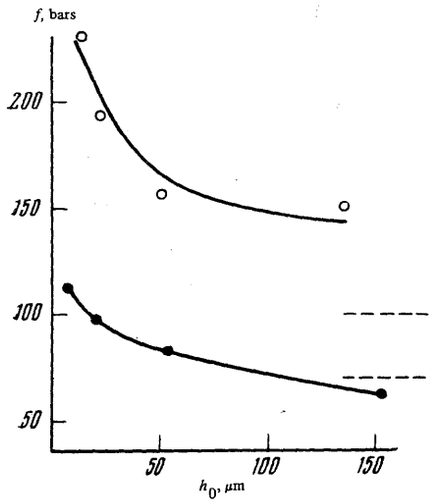


Figure 7. Resistance to rupture of "glass — purified polyethylene — glass" adhints (upper curve) and "steel — purified polyethylene wax — steel" adhints (lower curve). Abscissa—thickness of the layer of adhesive in micrometers. Ordinate—breaking strength in bars. The dotted lines indicate the tensile strength of the free polyethylenes.

Fifthly, the accumulation of the impurity near the surface and hence the formation of a weak boundary layer was eliminated by increasing the solvent power of solid polyethylene[15]. Petrol and water are almost immiscible, but their complete mixing can be achieved by adding sufficient acetone. By analogy, when polyethylene is treated with a substance soluble in solid polyethylene and capable of dissolving oleic acid, the acid will cease to accumulate in the surface layer and to reduce the strength of the adhesive joint. Ethyl palmitate $C_{15}H_{31}COOEt$ was found to be such a substance. The breaking stress for specimens with a "pin" was less than 1 bar when the adhesive was a mixture of 99 parts of polyethylene and one part of oleic acid, while the adhesive consisting of 94 parts of polyethylene, one part of oleic acid, and five parts of palmitate was ruptured following the application of a stress of 75 — 95 bars, i.e. was almost equal to the resistance of the purified polymer.

This example is particularly instructive if it is compared with the predictions of the molecular theory of adhesion. According to this theory, polar molecules increase adhesion. In fact polar oleic acid caused a catastrophic decrease of f; ethyl palmitate, the dipole moment of which is equal to that of oleic acid, does not alter f at comparable concentrations in purified polyethylene and its admixture in polyethylene contaminated with oleic acid sharply increases f. The resistance to rupture depends on solubilities and not on polarities.

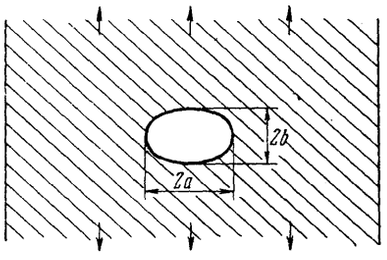


Figure 8. Concentration of stresses at an elliptical opening in the film. Axes of the ellipse—$2a$ and $2b$.

In the disintegration of systems containing weak boundary layers of the second kind, part of the layer remains on the adhesive and the remainder on the adherend. This separation has been demonstrated by simple weighing[13] and by electron microscopic observations[16].

It is clear from the foregoing that the formation of weak boundary layers of the second kind may be prevented either by removing harmful impurities from the adhesive or by increasing their solubility in the solid polymer. The third method is widely used in industry: impurities are decomposed by oxidation or by some other chemical reaction. In the fourth method they are polymerised. Polyethylene is subjected to an electric discharge in helium or another inert gas[17]. This results in the cross-linking of short molecules on the surface layer, which sometimes becomes several times stronger than the main bulk of the adhesive. Adhesive joints with such polyethylenes are ruptured in the polyethylene and for them f is determined by the strength of the polymer.

Other examples of weak boundary layers of the second group were apparently observed by Buiko and Zinchenko[18], Foster and Winn[19], etc.

3. Weak boundary layers on the adherend are also a common phenomenon. The aim of the cleaning of metallic surfaces before varnishing, enamelling, etc.[20] is to remove such layers. Since chemical contamination of the surface does not impair its mechanical properties, cleaning is unnecessary: adhesive joints with aluminium are formed daily and can be maintained indefinitely although the surface of the metal is covered by a continuous oxide film from edge to edge.

The effect of a random contamination of the metallic surface on the strength of adhints has been described in Buchan's book[21]. The attachment of rubber to brass is frequently performed in industry but is sometimes unsuccessful. Buchan studied the surface of electrolytic brass

specimens to which it was difficult to attach rubber. The complex salt $[Zn(NH_3)_6]\{Zn_3[Fe(CN)_6]_2\}$, which probably in fact formed the weak zone, was detected on some specimens. Theoretically, the cyanide electrolytes from which brass was precipitated contain no iron but sufficient iron ions entered the bath from the tubes and instruments employed in the manufacture to make possible the synthesis of the above salt.

The effect of adhesive butt joints of the type "steel — epoxy-resin — dye — tinplate — epoxy resin — steel" was investigated as a function of the purity of the tinplate[22]. Stearic acid deposited on the plate in an amount of 0.004 mg per cm^2 reduced the resistance to rupture f by 30 — 40%; when the surface concentration of the acid was raised to 0.04 mg cm^2, f was 50% below the value for the clean plate. In the presence of contaminations, the rupture surface passed along the boundary between the dye and the tinplate, i.e. in a weak boundary layer.

An example of a non-metallic surface is mentioned by Kamenskii[8]. The attachment of an unvulcanised rubber mixture to old vulcanised rubber yields adhints with low values of Γ. If the brittle and oxidised surface layer of vulcanised rubber is removed by brushing with a wire brush, the breaking stress increases, say, by a factor of 6.

A later example refers to polypropylene[23]. A double metallic plate — epoxy-resin — polypropylene film — epoxy-resin — metal adhesive lap-joint was ruptured readily and the rupture surface did not differ in any way from the initial surface of polypropylene. However, it was sufficient to treat the film with trichloroethylene vapour for several seconds to increase the resistance to rupture by a factor of 6 and to shift the rupture plane from the surface to the bulk of the film.

Industrial polycaprolactam apparently constitutes an even more striking example of weak boundary layers than polypropylene or polyethylene. It contains up to 12%, of the monomer[24], which is seen on certain films as a crystalline deposit. As long as the monomer is present on the surface of the polymer, neither polychloroprene nor polyisobutylene (deposited on a fabric ribbon) form strong adhints with polycaprolactam; however, the resistance (Γ) to rupture increases several times after the extraction of the monomer with water[25]. Unfortunately the authors did not compare the experimental Γ with the theoretical values, so that the reader finds it difficult to judge how complete the purification of polycaprolactam has been. Different elastomers form with unpurified polycaprolactams adhesive joints which have different resistances Γ. It would be instructive to compare the sequence of these elastomers in terms of increasing Γ with their sequence in terms of increasing capacity to dissolve the monomer; possibly the two series will be similar.

4. A weak boundary layer formed on interaction between the adhesive and the medium was observed when purified polyethylene was employed as the adhesive. As already stated, all polyethylene adhints described in section III, 2 were formed in an atmosphere of nitrogen. When similar adhints are prepared in air, polyethylene is oxidised (becomes yellow) at a high temperature and the oxidation products form a weak boundary layer, so that the strength of the adhint decreases.

5. Weak boundary layers of the *fifth group* are formed most often when an adhesive joint prepared in an inert medium is then introduced into a corrosive environment. Silicate glasses swell in water. Glass filaments in glass laminates also swell if the access of water to them is not prevented. Swollen glass is a weak material; in glass laminates ruptured underwater the crack usually arises in the swollen interfacial layer. Bitumen protects aluminium from corrosion simply by preventing the access of water to the metal. If water nevertheless reaches it, a phase, which may be called an aluminium hydroxide gel, gradually grows between the metal and the protective coating and bitumen is readily separated from aluminium[26].

In both examples just quoted the mechanical effects of swelling probably play a decisive role. The specific gravity of swollen glass is lower than that of dry glass and the specific gravity of aluminium hydroxide is lower than that of the metal. Thus a weak boundary layer splits the adhesive away from the adherend like a wedge. Unfortunately this mechanism has not yet been subjected to mathematical analysis.

It may be that swelling also weakened adhesive lap joints of the type "aluminium — epoxy-resin — aluminium", which were prepared in various atmospheres and were allowed to remain in the same medium for 1 h.[27] After such ageing, their f values were measured. In dry argon the resistance was only 5% lower than before ageing but in an atmosphere comprising 80% of argon and 20% of oxygen with a relative humidity of 50%, ageing reduced f by a factor of 2.

6. Weak boundary layers of the *sixth kind* are formed most frequently when the adhesive reacts chemically with the adherend. Long ago it was already noted that a highly alkaline casein glue forms weak adhesive joints of the type "wood — glue — wood". Alkali corrodes (hydrolyses) wood and gives rise to a weak zone between the adhesive and the unaffected wood. Clearly similar difficulties arise if an acid adhesive is employed to cement copper, zinc, iron, and other metals sensitive to acids. Less obvious examples are also known[28].

When rubber is vulcanised on brass, the joint will be weak in those cases where the brass surface is immaculate (see section III, 3). In many cases it is sufficient to introduce an excess of sulphur into the rubber mixture (for example 10% instead of 2%); the excess sulphur reacts with copper in the brass and forms copper sulphide, which is segregated in the form of a powder between the two main phases[21]. The excess sulphur may be harmful also in the absence of copper. A mixture of sulphur and raw natural rubber was placed on the surface of a synthetic vulcanised rubber, the entire system was heated, cooled, and the film of natural rubber (now vulcanised) was peeled off. The resistance to peeling fell when the system was heated too long; probably sulphur diffused from the mixture to vulcanised rubber and increased the brittleness of its surface layer[29].

The examples just quoted are particularly instructive, since there are still investigators[30] who believe that the chemical bond between the adhesive and the adherend may be the cause of strong adhesive joints. It is much more likely that the chemical reaction weakens the adhint instead of stabilising it.

The chemical reaction yields a new substance which is frequently insoluble in the starting materials and is independent of them; it is neither willing nor able to couple, in the words of Lucretia, the two adjacent phases.

The adhesive and the adherend do not form weak boundary layers solely via chemical reactions; sometimes diffusion is also sufficient. Two relevant examples will be quoted.

If a metal K in contact with a metal M is heated, the diffusion of the atoms of K into the lattice of M may be faster than the diffusion of M into K. Then cavities

remain in the metal K near its boundary with M; initially they are of atomic dimensions but subsequently they merge into pores, which are visible under the microscope. In other words, a weak boundary layer is produced. It was noted[31,32] on prolonged heating (25 days at 800°C) of a copper plate coated with brass or aluminium bronze (93% Cu, 7% Al). Cavities with diameters up to 0.001 cm were observed in these alloys at the very boundary with copper.

Gold filaments welded to aluminium were difficult to tear off and the rupture apparently occurred along the boundary between the two metals. In order to elucidate the mechanism of the phenomenon, the system was maintained at 450°C for 2 h and then the transition layer between aluminium and gold was investigated[33]. It was found to contain seven phases: aluminium, $AuAl_2$, AuAl, Au_2Al, Au_2Al_2 (?), Au_4Al, and gold, and numerous pores were visible along the boundary between the Au_5Al_2 (?) and Au_4Al phases. The crack spread in the region of the pores and not between the two different metals. This example too is instructive. Supporters of the molecular theory of adhesion would calculate the attraction between the ideal crystals of gold and the ideal crystals of aluminium in an ideal contact and would compare the adhesion thus calculated with the experimental strength of the weld. How remote is reality from academic theories!

7. All three phases present in the formation of the adhint participate in the creation of weak boundary layers of the *seventh group*. Such systems were studied by Black and Blomquist[34]. When the adhesive lap joint consisted of an adhesive and two aluminium plates, the breaking stress at room temperature was approximately 122 bars. The adhesive was a mixture of eight parts of phenolic resin and one part of epoxy-resin. After the system had been heated (288°C) for about 100 h, f (still at room temperature) decreased to 65 bars, so that the system may be regarded as comparatively temperature resistant. The strength of adhints of the same dimensions but with stainless steel adherends was fully comparable, before heating, with the value of f for aluminium joints, but after heating f was negligibly low. In order to reduce f almost to zero, the system had to be heated in air or oxygen; heating in nitrogen had little influence on f. The authors concluded that a component of stainless steel accelerates the oxidation of the adhesive by gaseous oxygen, i.e. catalyses the reaction. Systematic experiments showed that copper, the classical accelerating agent for the oxidation of organic compounds, is responsible.

The disintegration of the adhint began at a three-phase boundary where air, the adhesive, and the metal meet; a visible strip of oxidised adhesive gradually spread along the metal surface. All three phases were involved in the formation of a weak boundary layer: the layer did not arise when the metal contained no copper or the gas contained no oxygen and when the adhesive was a polyamide or a butadiene — acrylonitrile copolymer.

What lesson can we draw from this section? Along the boundary between the adhesive A and the adherend B, there are in many systems weak materials, different from both A and B; cleavage or rupture occur within the bulk of these materials. If the experimenter does not suspect their existence, he may decide that the disintegration was of the adhesive type, i.e. that the crack occurred exactly between A and B and that his task may be to strengthen the mutual attraction between these two substances. In fact he must discover with what kind of weak boundary layer he is dealing (the first group? the second group?...) and how the formation of such a layer can be prevented. Weak boundary layers can never be disregarded with impunity.

IV. LOCATION OF RUPTURE

The concept of weak boundary layers permits a more critical approach to the main problem of adhesive joints already discussed from the theoretical standpoint in the first section of the review. If the rupture of the adhint is seen with the naked eye to occur along the interface, the question arises of whether one is dealing with an adhesional failure or a cohesional rupture of a weak boundary layer. As just stated, the answer to this question is extremely important: the entire plan of future work on the improvement of adhints depends on it.

The conclusion that the rupture of adhesive joints hardly ever occurs exactly between the adhesive and the adherend has unfortunately been confirmed by only a few experiments undertaken to test it. It is difficult to make such experiments convincing. Generally speaking, molecular forces decrease very rapidly with distance from a given molecule or a given solid. The molecular attractive forces between two bodies A and B may be neglected compared with the forces between A and C and between C and B when the thickness of the third substance C between A and B exceeds several ångstroms; the majority of studies leading to the opposite conclusion are based on an erroneous interpretation of experimental data. Thus one can assert that experimental results confirm the above conclusion even if the residual adhesive (or one of its components) on the adherend after rupture is not thicker than several ångstroms; in other words, the monomolecular third substance on the rupture surface of the adherend already demonstrates that the failure was not adhesional. The molecular layer of the adherend (or one of its components) on the surface of the adhesive after rupture is of course also instructive.

Analytical detection of monomolecular layers on the surface of a solid is very laborious. Methods whereby it is possible to detect surface contaminations with a thickness of 100 or 1000 Å may prove to be unsufficiently precise. This remark, applies, for example, to luminescence analysis, whereby it is possible to demonstrate transition layers (at the boundary between two polymers) with a thickness of 1 μm [35] and which clearly reveals the difference between an uncontamined surface and a surface coated with a film having an average thickness of 10 μm.[36] Unfortunately the difficulties are not confined to purely analytical problems. In many cases it is not known what should be sought. If, for example, there is a weak boundary layer of the second kind, the impurities migrating onto the adherend may be chemically quite different from the main component of the adhesive. Thus, after the rupture of an aluminium — polyethylene adhint, not even a trace of polyethylene was detected on the metal but this does not imply that the rupture occurred exactly along the boundary: we may suppose that, instead of the polymer, the antioxidant added to the polymer passed onto the adherend and since the experimenter did not look for it at all he did not find it. The situation is even worse in the case of weak boundary layers of the first group. If before rupture air occupies a considerable proportion of the interface, it cannot be distinguished from the air which penetrated the space between the adhesive and the adherend at the instant of rupture. Here the presence of a weak layer must be inferred from the breaking stress f. We shall suppose that an adhesive which wets freely an adherend B_1 forms with the latter adhints the value of f for which is 100 (in terms of arbitrary units). If the same adhesive in an adhesive joint of the same type and of the same dimensions gives $f = 1$ with an adherend B_2 and no traces of the adhe-

sive can be detected on the rupture surface of B_2, one can conclude with a considerable degree of certainty that a layer of air almost separated B_2 from the adhesive even before the rupture of the adhint.

We shall consider five experimental studies on the mechanism of apparent adhesional failure. Huntsberger[37] treated ribbons of an alkyd resin (with a thickness of 4 μm) with a solution of polyisobutylene from which a film approximately 25 μm thick was obtained after evaporation of the solvent and then one ribbon was peeled from the other. The thickness of the alkyd film after rupture was the same as initially. This result is unconvincing, since it was not shown how the solvent affected the alkyd film—whether or not it became stretched during rupture, whether a certain amount of the alkyd resin remained on polyisobutylene, and what was the effect of the surface roughness on the measured thickness.

Johnson[38] rubbed the rupture surface with a potassium bromide powder and measured the infrared spectrum of the powder scraped off the surface. If the powders from the surfaces of the adhesive and the adherend were identical, then clearly the rupture occurred in a particular material and not *between* two different materials. This happened, for example, when a varnish film (of unknown composition) was deposited from solution onto an organic adherend (also insufficiently characterised). The resistance to rupture was very low and both spectra showed absorption lines due to the phthalate esters employed as plasticisers. Evidently the failure, which at first sight appeared to be typically adhesional, consisted in the splitting off of a surface phthalate film. When polymers without a plasticiser were employed, both spectra were still almost identical. They corresponded to one of the polymers slightly contaminated with the other. In a third system, a dye, i.e. plastic + pigment, was coated with the solution of another polymer. After drying and peeling, the spectra were found to be different. Unfortunately none of the above systems was investigated in detail. Four tacky plasters were clamped to five adherends, were peeled from them at two different rates, and the contact angles θ of a drop of water in air (at 50% humidity) on the adherend were determined[39]. Of the 49 results obtained, only four are quoted here; the changes in contact angle were in the same direction as in all other systems. The angle θ on glass was 11° before contact with the plaster. When the plaster was stripped off rapidly, $\theta = 36°$ was obtained; after slow peeling, θ was 44°. Water on the plaster gave $\theta = 92°$. Thus θ changed in all cases in the direction from the adherend to the adhesive and was closer to θ for the adhesive when the peeling was slow and there was more time for the adhesive to displace air from the hollows on the surface of the support. In this study measurements were made of the contact angle of water which one must suppose did not alter (or only slightly altered) the properties of the organic adhesive (polyacrylate in the preceding example). It is incorrect to employ for the estimation of wettability liquids which are good solvents of traces of the adhesive remaining on the adherend. Clearly a drop of solvent in a volume of perhaps 1 cm^3 very rapidly removes contaminations weighing 0.000001 g per square centimetre[40].

If the adhesive contains labelled atoms, its traces on the support after rupture can be comparatively readily determined[41]. Aluminium plates were covered with a solution of polyurethanes, the solvent was removed at 60°C over a period of 16 h, and the polyurethane films were peeled from the metal. When the average roughness of aluminium was 0.76 — 1.02 μm, the average thickness of the residual adhesive on it was approximately 200 Å and for a roughness of 0.38 — 0.51 and 0.13 — 0.25 μm, the average thickness of the contaminant τ was 120 and 80 Å.

In the most valuable investigation, the thickness of the residue and the resistance to rupture Γ were measured on the same specimens[42]. Radioactive polypropylene was clamped to glass at 60°C and then peeled at room temperature. When the duration of contact at 60°C was 10 min, Γ amounted to 113 kdyn cm^{-1} and the thickness τ was equivalent to 2.4 monomolecular layers; after 60 and 120 min of contact, Γ was 236 and 226 kdyn cm^{-1} and τ was equivalent to 3.4 and 5.5 monolayers. Consequently, as long as τ remained small, τ and Γ increased together. One may conclude that $\tau = 0$ only when $\Gamma = 0$; when the adhesive is separated from the support without leaving a residue, no force is required for the rupture.

The electron microscope has so far proved relatively unsuitable for the determination of τ. The reason is that usually the method of replicas has to be employed. Traces of adhesive on the adherend may dissolve in the polymer from which the replica is made or in its solvent; in all such cases the material in which the experimenter is interested becomes invisible. Even if one chooses for the replica a high-molecular-weight compound which does not mix with the adhesive, one cannot rely on the pattern obtained. The general scientific principles of adhesion are applicable to replicas as well as to any other coating. If the replica comes into true molecular contact with the adherend, it cannot be separated from it exactly along the interface. The replica can be stripped readily only if there is never any true contact. It may be that the surface of the replica which before peeling was directed towards the adherend does not reproduce its profile in all details. The differences may be insignificant in those cases where an error of 100 or 200 Å is acceptable but the method is inapplicable when monolayers are considered.

V. PROPER ADHINTS

Improper adhints are frequently encountered in the laboratory but fortunately they constitute a rare exception among adhesive joints produced industrially on a large scale. In proper joints failure occurs either in the bulk of the adherend or in the bulk of the adhesive; there is no doubt that it is "cohesional" and not "adhesional". With the exception of a negligible percentage of adhints deliberately ruptured in laboratory tests, proper joints may be said to be immortal. An old table or an old aeroplane is scrapped when the adhesive joints between the leg and the frame in the first object or between two pieces of aluminium in the second are still in an excellent state. The deterioration of other components made the whole object valueless.

If the adherends in adhesive joints are made of metal or glass and the adhesive is an organic polymer, failure occurs much more often in the bulk of the adhesive than in the bulk of the adherend. Henceforth it will be assumed that the adhesive always breaks. The adherends in proper joints have no pores in an amount sufficient to assign the adhint to the hook type described in the second section; only in rare cases is it difficult to decide to which type the given adhint belongs.

Since rupture occurs in the adhesive, the measurement of the resistance to rupture of a proper adhint reduces essentially to the measurement of the tensile strength f_M of the adhesive. This strength can be of course found quite independently of any adhesive joints. It would

appear that f_M is a characteristic property of the polymer such as its density or chemical structure; it would also appear that the resistance to rupture f of the adhint is always identical with f_M of the given adhesive. In such a case there would be no need to measure f; the strength of all adhesive joints made with a particular adhesive would be equal to the tensile strength f_M of the polymer. In fact f_M is not a very constant quantity and f usually differs appreciably from f_M. The approximate equations

$$f = \frac{1}{\alpha}\left(\frac{\xi}{\beta} - s\right) \qquad (2)$$

and

$$f_M = \frac{\xi}{\beta_M} - s_M \qquad (3)$$

probably provides the clearest illustration of the foregoing statement. Here ξ denotes the theoretical cohesion of the adhesive, β and β_M are the stress concentration factors due to the inhomogeneity of all solids, α is an analogous factor due to the difference between the mechanical properties of the adhesive and the support, and s and s_M are residual stresses. Only ξ is the same in both equations; β is not necessarily equal to β_M and s may differ from s_M. The longest section of the author's book[2] is devoted to the difference between f and f_M which, incidentally, is pointed out at the very beginning of the present review; below this difference is discussed in an abbreviated form.

1. The factors β and β_M are equal to the ratio σ_m/σ in the layer of adhesive and in the free rod of the adhesive; as in the first section, σ_m is the maximum "local stress at a square" and in the bulk of the material and σ is the stress averaged over the entire cross-section of the specimen.

If in a solid sheet or in a solid film there is a fairly wide elliptical aperture (Fig. 8) located in such a way that the major axis of the ellipse ($2a$) is perpendicular to the external force (indicated by arrows) and the minor axis ($2b$) is parallel to it, then the stress τ_m at the right-hand and left-hand edges of the ellipse is

$$\sigma_m = \sigma\left(1 + \frac{2a}{b}\right). \qquad (4)$$

Numerous formulae for apertures of more complex shapes are quoted by Savin[43]. If the ellipse is greatly extended, i.e. resembles a crack, the ratio $2a/b$ should be very large. For example, if $a = 100b$, then σ_m/σ, i.e. the stress concentration factor β is 201. In such cases, even when the average stress σ is quite inadequate to overcome the cohesion ξ of the material, the stress σ_m may prove to be greater than the cohesion and consequently can cause the growth of the crack and the rupture of the specimen.

Clearly the probability of encountering an aperture for which the ratio a/b is large enough to give $\sigma_m > \xi$ is greater the larger the specimen. This is one of the main reasons and perhaps the most important reason for the increase of f when thinner films of adhesive are employed, as shown in Fig. 7. The greater the bulk of the adhesive, the greater the maximum value of the a/b ratio.

2. Butt joints. The coefficient α depends on the geometry of the system. Adhesive joints between the end-faces of two rods or pins would appear to be most suitable for the determination of the breaking force having a general significance. If the cross-section of the rod is S (cm²) and the external force required for rupture is F (dynes or newtons), one might conclude that the stress giving rise to the growth of a crack is F/S. Such a conclusion would be erroneous.

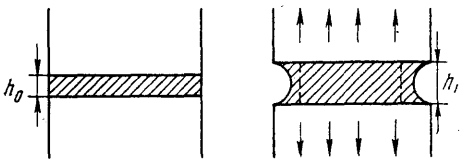


Figure 9. Concentration of stresses induced by the deformation of an adhesive "fillet". Left-hand diagram—butt joint before stretching; thickness of "fillet"—h_0. Right-hand diagram—ditto after stretching; thickness—h_1.

Fig. 9 illustrates a typical adhesive butt joint. The thickness of the adhesive layer has been increased by a factor of 20 in order to show more clearly its deformation on extension of the system. The left-hand and right-hand diagrams illustrate the system respectively before and after extension almost to rupture; the modulus elasticity of both rods is assumed to be so high that a change in their shape may be neglected. When the external force (arrows!) extends a flat cylinder of adhesive, its radius diminishes; this is Poisson compression. Fig. 9 shows that the compression cannot be homogeneous, since the adhesive is attached to adherends and its layer adjoining the adherends cannot be compressed as long as the adherends are not compressed. If this limitation did not exist, the profile of the adhesive cylinder would be as shown by the dashed line. Its true profile is indicated by the continuous curve. Clearly the cylinder is "unnaturally" extended not only along its axis but also in a perpendicular direction; it may be that both tensile and compressive stresses operate in it and the true stress σ at each point must be calculated from the theory of elasticity (or on the basis of more complex theories if the adhesive does not obey Hooke's law). This calculation has probably not as yet been performed with sufficient accuracy but the effect of the deformation of the adhesive on the distribution of stresses may be estimated roughly on the basis of the three special examples discussed below.

Suppose that the thickness of the adhesive before extension were h_0 and in the extended state h_1. We postulate that the profile of the extended cylinder is fairly close to an ellipse, the vertical half-axis of which is evidently $0.5\,h_1$; the horizontal half-axis is designated by the symbol a. We also postulate that the system was heated before deformation, so that its residual stresses s were reduced to zero. Then the volume of the adhesive will be also almost equal to the initial volume $\pi r^2 h_0$, where r is the radius of the adherend and of the initial "fillet" of the adhesive. It follows from the equality of the volumes that the half-axis a is

$$a = \frac{2r}{\pi} \cdot \frac{h_1 - h_0}{h_1}. \qquad (5)$$

On substituting this value of a in Eqn. (4) remembering that $b = 0.5\,h_1$ in this equation, we find that the stress at the

bottom of an elliptical hollow is greater than the average value by a factor α and that

$$\alpha = 1 + \frac{8r}{\pi} \cdot \frac{h_1 - h_0}{h_1^2} \quad (6)$$

Thus a purely geometrical departure of the layer of adhesive from the initial shape is sufficient to determine the stress concentration. For example, if $r/h_1 = 100$ and $(h_1 - h_0)/h_1 = 0.1$, then $\alpha = 26$. The greatest stress in the system is 26 times larger than F/S.

The above hypothesis that the layer of adhesive is free from residual stresses is invalid in the usual tests on adhesive joints. Almost always two opposed forces act along the boundary between the adherend and the adhesive. The adherend attempts to extend the adhesive in a radial direction and the adhesive attempts to reduce the radius of the adherend. If both materials obey Hooke's law and the modulus of elasticity of the adherend is many times greater than the modulus of the adhesive, the tensile stress P (g s^{-2}) acting per unity length of the boundary between the adhesive and the adherend is to a first approximation[2]

$$P \simeq \frac{h_1^{1.5} f}{2r^{0.5}} , \quad (7)$$

where h_1 and r have the previous values and $f = F/S$. Suppose that h_1/r is again 0.01; then $P \simeq 0.05\, h_1 f$. When the thickness of the adhesive layer (in the extended state) is 0.1 cm, $P \simeq 0.005\, f$ (g s^2). This tensile stress is distributed throughout the thickness of the layer, which is determined by the roughness of the interface. In this case, when the average roughness dimension is about 1 μm, the radial stress is not far from $50\, f$ (g cm^{-1} s^{-2}). In this example the maximum stress is not observed at the bottom of the elliptical hollow but at its boundary with the adherend and exceeds the average stress by a factor of 50. Its experimental estimate may be found in the paper by Mylonas[44].

Eqns. (6) and (7) are applicable, since Hooke's law holds for all parts of the system. If the adhesive is an ideal plastic material, i.e. is not deformed at all as long as the shear stress is below a characteristic value (kg cm^{-1} s^{-2}), and flows freely when the stress exceeds k, then

$$f = \frac{wk}{h_0} , \quad (8)$$

for an adhesive joint consisting of two rigid plates with a width w (cm) and a layer of adhesive with a thickness h_0 (cm). If the adherends are cylinders with a radius r, then[45]

$$f = \frac{2kr}{3h_0} . \quad (9)$$

It is remarkable that f is inversely proportional to the thickness h_0. Adhints with a very thin layer of adhesive should have an enormous strength when plastic adhesives are employed; this conclusion has been confirmed experimentally, for example by Mossatt and Wulff[46]. The effect of the thickness h on the strength of such systems is much greater than for the purely elastic adhesives discussed in section V, 1.

In principle, the critical shear stress k is a constant of the material of the same kind as the cohesion ξ. Eqns. (2), (8), and (9) show that the breaking stress f is never equal to ξ or k even when the rupture undoubtedly takes place within the bulk of the adhesive. The path from molecular forces to resistance to rupture is long and thorny.

3. Lap joints. It would appear that when the upper plate of the adhesive joint illustrated in Fig. 10 is pulled to the right and the lower plate to the left, purely tangential stresses (shear stresses) will arise in the layer of adhesive between both plates. In fact the distribution of stresses is much more complex in this case also.

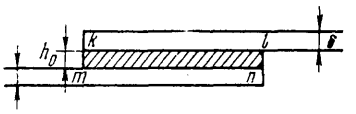


Figure 10. Concentration of stresses in a lap joint.

Firstly, the lines of force should undergo a sharp change of direction on passing from the upper plate to the adhesive and from the adhesive to the lower plate. Therefore near the points k, L, m, and n, there is a concentration of stresses analogous to that which arises at the corners of a square cut in a sheet or a film (instead of the ellipse shown in Fig. 8). The coefficient α of this concentration increases as the ratio of the thickness h_0 of the adhesive layer to the thickness δ of the solid plate diminishes; in the usual adhints α may easily reach values of 10.

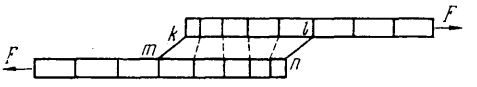


Figure 11. Differential stretching of plates in a lap joint.

Secondly, the external forces (arrows in Fig. 10) extend the plate unequally along its length, so that the film of adhesive is not only extended but also bent. This is illustrated in Fig. 11. To the right of the point l in the upper member and to the left of the point m in the lower member, the entire force F acts on the plates and their relative deformation is high. At the points k and n, i.e. at the free ends of the plates, there can be no stress. It may be that the relative deformation gradually diminishes from l to k and from m to n, as shown schematically in Fig. 11. If both the plates and the adhesive obey Hooke's law, it is possible to derive an approximation expression for the maximum coefficient α of the concentrations of tangential stresses at the ends of the layer of adhesive:

$$\alpha = \left(\frac{G_1}{2E\delta h_0}\right)^{0.5} L , \quad (10)$$

where G_1 is the modulus of shear elasticity of the adhesive, E the modulus of elasticity of the adherend on extension, δ the thickness of the plate, h_0 the thickness of the adhesive, and L the length of the overlap, i.e. the distance $\overline{kL}$ or $\overline{mn}$. Since the dimensionless ratio $L/(\delta h_0)^{0.5}$ reaches 100 in many adhints, the coefficient α due to the deformation under consideration may sometimes be actually higher than the coefficient calculated above.

Thirdly, plates are bent when an external force is applied, as shown in Fig. 12. The left-hand side shows a system subjected to a force so weak that deformation is still not observed. Clearly the force pulling one of the plates upwards does not act along the same line as the force equal in magnitude and pulling the other plate downwards. A twisting moment is generated, which leads to the deformation shown on the right-hand side of the Figure; here both forces act along the same straight line but the two plates are bent. The deformation of the plates causes the deformation of the adhesive between them. Evidently the distance between the adherends near the points m and n is greater than in the centre of the adhesive film, so that the adhesive is extended not only in the vertical direction but also its thickness near the ends is appreciably greater than before and greater than the thickness of the middle sections in the present case. The stresses in the adhesive near the ends of the film are similar to the stresses responsible for peeling (see section V, 4).

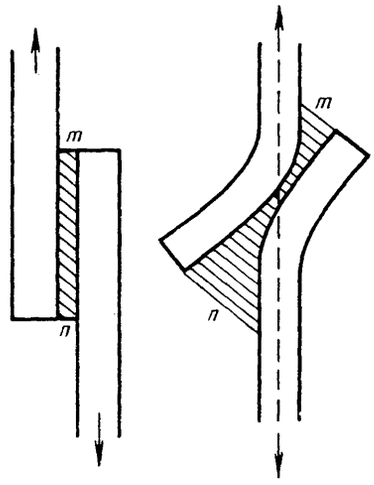


Figure 12. Bending of the plates in the stretching of a lap joint. Left-hand figure—low external force. Right-hand figure—high external force.

Their theory was developed by Goland and Reissner[47] and was tested in detail by Henning[48].

If the plates are appreciably bent, the stress in the adhesive is much greater at the ends of the film than in the centre. Therefore the middle parts of the film carry almost no load and may not be necessary. This conclusion has been confirmed experimentally[49]. When the space between two plates was filled with an adhesive along a 2.5 cm section, the resistance to rupture F was 1.3×10^9 dyn (or 1.3×10^4 newtons). When the middle half of the layer was left unfilled, i.e. the section with a length of 2.5 cm contained 0.625 cm of adhesive + 1.25 cm of void space + 0.625 cm of adhesive, F was still 1.1×10^9 dyn (or 1.1×10^4 newtons). In other words the removal of half the adhesive from the centre reduced F by only 20%. Fig. 13 presents more results[50] of the same kind. Two aluminium plates 25 mm wide and 1.5 mm thick were glued together over a section 20 mm long. The end of this section were in all cases filled with glue but in the centre there remained a void, the length of which was varied from 4 to 16 mm. This length is plotted along the abscissa in Fig. 13, the ordinate representing the stress f sufficient for rupture; it is expressed in bars. The lower curve was calculated disregarding the voids; evidently, when the length of the unfilled slit was 12 mm, i.e. 60% of the total length, f was hardly less than the resistance of a continuous film of adhesive. Calculation of the stress for the filled part of the slit yields the upper curve.

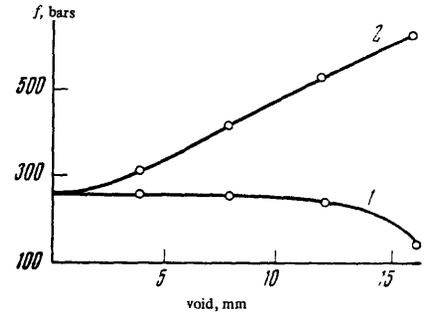


Figure 13. Effect of a cavity in the surface of the adhesive film on the strength of the lap joint. Abscissa—length of the void in millimetres. Ordinate—shear resistance in bars: 1) resistance calculated for the entire length; 2) resistance calculated for the filled section.

The coefficient α, calculated in accordance with one of the previous theories, must be introduced into the general Eqn. (2) in order to obtain some idea of the resistance to shear which may be expected from the given system. For example, α may be found from Eqn. (10), since the geometrical parameters (δ and h_0) of the system and the principal mechanical constants (G_1 and E) of the materials are known. If s_M in Eqn. (3) is low, the transient resistance of the free adhesive film (f_M) is almost equal to the ratio ξ/β. If s is also small in the given adhesive joint, then $f \simeq \xi/\alpha\beta \simeq f_M/\alpha$. For lap joints, $f = F/wL$, where F is the applied force and w and L are the width and length of the adhesive layer (which is of course continuous). We obtain finally

$$F = wLf_M/\alpha \ . \qquad (11)$$

Under favourable conditions F may be predicted, provided that w, L, δ, h_0, G_1, E, and f_M are known. If the most dangerous concentration of stresses is not a result of differential stretching but is a consequence of Eqn. (9) or the flexibility of the plates, other expressions for α must be introduced into Eqn. (2), but the equation itself remains in force; F continues to depend only on f_M and the geometry and mechanical properties of the components of the adhesive joint.

4. Peeling. An adhint subjected to peeling is illustrated in Fig. 1. The horizontal distance ζ between the point of application of the force and the edges of the adhesive "fillet" (at which the arrow from the letter G terminates) greatly influences the peeling resistance but unfortunately so far it has not been possible to calculate it convincingly on the basis of the dimensions and mechanical

constants of the components. In those cases where the flexibility of the ribbon is very high (for example, when a thin metallic foil serves as the adherend), the distance ζ can be virtually neglected. When $\zeta = 0$, there is a simple formula[51] for the minimum force F necessary for peeling:

$$F = kwf_M (E_1/E_1)^{0.25} \delta^{0.75} h_0^{0.25} . \quad (12)$$

In its derivation, it is assumed that the adhesive and the ribbon obey Hooke's law and therefore have unique values (E_1 and E) of the modulus of elasticity. As before, the width and thickness of the ribbon are denoted by the symbols w and δ, the thickness of the layer of adhesive is denoted by h_0, the transient resistance of the molecule by f_M, and the numerical factor $K = 0.38$ when the Poisson factor $\nu = 0$ for both components and $K = 0.76$ when $\nu = 0.33$ in both cases. The rigid adherend is assumed to be completely incapable of being deformed.

The accuracy of Eqn. (12) is of the same order as that of the equation $f = F/wL$ mentioned above, i.e. it disregards both the residual stresses s and the factor α. If, for example, $\alpha = 5$, the values of the force F predicted by Eqn. (12) will be five times higher than the experimental quantities. Inconsistencies of this order of magnitude were observed in the peeling of an aluminium foil glued to glass with purified polyethylene. Probably the maximum value of α is observed at the boundary between air, the adhesive, and the ribbon when the adhesive is brittle and at both ends of the adhesive film along the width w when the maximum relative extension of polyethylene is high. Incidentally, it was easy to show that considerable amounts of polyethylene were present on both rupture surfaces[13].

Equations analogous to Eqn. (12) could be derived also for the simplest cases of non-Hookean materials. Thus Fukuzawa[52] calculated Γ for peeling at an angle of 180° assuming that the adhesive is a viscoelastic substance obeying Maxwell's equation.

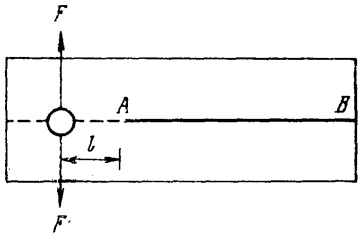


Figure 14. The splitting of two rigid bars glued along the AB plane. F = external force; L = length of crack.

Peeling theory predicts that, although the stress in the adhesive at the "leading" edge of the film (indicated by an arrow in Fig. 14) is a tensile stress, the stress somewhat to the right of the edge (in Fig. 14) changes sign so that there the ribbon is now clamped to the adhesive and compresses it. There is nothing unexpected in this phenomenon: if one end of a lever is pushed downwards, the other end tends to rise. The change in the sign of the deformation of the film was demonstrated by special measurements[53].

The direction of the external force F in Fig. 14 is perpendicular to the plane of the adhesive film. As already mentioned, the peeling angle need not be 90° (or $\pi/2$ radians). When the angle φ is altered, in certain systems [for example in poly(vinyl acetate) reinforced with silk and glued to glass], the force F is inversely proportional to $1 - \cos\varphi$, so that the work formed in peeling, which is $FL(1 - \cos\varphi)$, proves to be independent of φ; l is the length of the peeled section. In other systems the dependence of F on φ will be different for different rates of peeling. For various polyurethanes, the tension Γ for $\varphi = 90°$ was of 1.5 times or twice as high as for $\varphi = 180°$.[54]

When both adherends are rigid bars and are incapable of being bent, splitting is employed instead of peeling, as shown in Fig. 14. The work W which must be performed in the spreading of the crack within the layer of adhesive may be calculated from experiments of this kind. Usually W is proportional to the area S of the crack and the ratio W/S = "γ" is independent of S. For epoxy-resins, this "γ" was in most cases lower only by several per cent than the "γ" measured in the splitting of bars of the same epoxy-resin without any adhesive[55].

VI. DEPENDENCE OF STRENGTH ON EXTERNAL AND INTERNAL CONDITIONS

This section reviews the relations between the breaking stress f and specific resistance to peeling Γ on the one hand and the dimensions of the system, the chemical composition of the adhesive, and other conditions on the other; the results are explained from the standpoint of the author's "rheological" theory and at the same time from the standpoint of the molecular theory clearly presented in a recent review by Kardashev and Vakula[30] and in the book of Berlin and Basin[10].

1. Dependence on the method of measurement. The data in Fig. 7 were obtained for the rupture of butt joints arranged in such a way that the stress concentrations described in section V, 2 were virtually absent. When the adhesive layer was sufficiently thick, the resistance to rupture was almost equal to the tensile strength of the free adhesive in the form of a bar. The same adhesive (purified polyethylene) was employed in the peeling experiments described in section V, 4. The results were lower by a factor of 5 than expected from Eqn. (12); thus one might conclude that in the failure of geometrically different adhesive joints, different quantities are measured. As stated above, this conclusion is unjustified: experimental data do not confirm Eqn. (12) simply because it is valid only for the ideal case which departs widely from reality. So far specimens for peeling tests in which there are no lateral stress concentrations have not been found.

Instructive results were obtained on comparing butt and lap joints and joints subjected to a twisting moment[56]. Aluminium "pins" of different dimensions were attached to one another with commercial adhesives, the tensile strength f_M of which was in the range from 490 to 760 bars (in the free state). Depending on the diameter, the resistance of the adhints to rupture varied between 250 and 620 bars. We may recall that f_M is measured on specimens for which the factor α is identically equal to unity. Probably in the adhints of Winter and Krause the coefficient was about 1.2 — 2.0, i.e. their adhesive joints were designed so skilfully that the concentrations of stresses were lower than calculated in section V, 2. Lap joints in which the thickness of the aluminium plates was 0.1 cm and the length of the overlap 1 cm were ruptured at a stress F/wL = 250 bars. It is not known to what extent the

plates were bent during the measurements, but the "geometrical" concentration of stresses and the differential stretching of the adherends and the adhesive undoubtedly occurred and probably raised α to 490/250 or 760/250, i.e. 2 — 3. When two rings were glued together and a twisting moment was applied to them, the breaking stress was found to be 470 — 660 bars, i.e. α was only slightly higher than unity. The twisting of the rings was recommended many years ago as a rational method for the measurement of adhesive strength[57].

Two short steel cylinders were glued together with polysiloxane rubber and the same adhesive was employed to join two short tubes via their butt ends[58]. The systems with two cylinders were ruptured either by shearing one from the other or by turning one of them about their common axis, while the system of two tubes was ruptured only by means of a twisting moment. The stress f necessary for rupture depended little on the method of breaking employed and the plots of s as a function of the rate of rupture also proved to be almost identical for all three series of experiments. The absolute value of f increased together with the rate from 11 to 20 bars. Unfortunately the tensile strength of the polysiloxane employed was not measured; did it exceed 20 bar?

In all the experiments described in this section proper joints were employed and as far as is known the breaking stress f did not differ appreciably from the breaking stress f_M of the adhesive. The difference between f and f_M can be readily accounted for by the different values of the factors α and β. It is of course possible that the residual stress f in the adhesive layer was also not the same as in a free bar. The question arises if the molecular theory of the strength of adhesive joints can account for these results. Evidently the attractive forces usually quoted in books and papers on adhesion (dispersion forces, hydrogen bonds, etc.) in no way depend on the manner in which the adhint is broken, so that a purely molecular theory is in this case quite useless. The weakness of this theory is so evident that even its supporters had to acknowledge that the measured value of f depends on the stresses in the adhesive and on its strength. How can one estimate in this case the contribution by adhesive forces to the experimental value of f? If the type and number of functional groups on the surface of the adhesive and the adherend and their capacity to interact play a decisive role in adhesion, what part of the stress f of the tension Γ is determined by these parameters? Supporters of the molecular theory have not attempted to answer this question either; the correct answer, is, of course, none.

2. Dependence on the dimensions of the system. The effect of the thickness h_0 of the layer of adhesive on f and Γ has been frequently studied. Curves similar to those in Fig. 7 are typical for butt joints; in practice it was noted long ago that, "the thinner the adhesive layer the stronger the adhesive joint". Apparently Crow[59] obtained the earliest quantitative results. He joined together copper cylinders via their butt ends with the aid of a eutectic solder (tin + lead) and found that the thinnest layers of solder (0.02 cm) were a little less than three times stronger than thick layers (0.5 cm) and that the strength of thick layers was equal to the tensile strength (630 bars) of free rods of the same solder. The dependence of f on h_0 proved to be less pronounced but qualitatively similar for steel cylinders glued together with poly(vinyl acetate)[60] and several other systems.

In the first place it is necessary to show whether this effect of h_0 on f is real. After all, in the extension of adhints at a constant linear rate dh/dt (t is the time and h the variable thickness of the layer of adhesive), the relative deformation, i.e. $(h - h_0)/h_0 = \epsilon$ increases more slowly, the greater h_0; clearly $d\epsilon/dt = (dh/h_0)dt$. It may be that the thicker the adhesive layer, the slower its deformation for dh/dt = const. Since f decreases in many cases when the deformation is slower, the dependence of f on h_0 may be only apparent. Accurate experiments which would make it possible to dispel these doubts once and for all have not apparently been made, but the increase of f with $1/h_0$ is observed in such a wide variety of systems that it is reasonable to regard it as a real phenomenon.

Then the question arises of its causes. One of the causes, which has long been the subject of quantitative tests[61], is described in section V, 1. In those cases where the layer of polymer at the boundary with the adherend has a higher strength than the free polymer[62], one may imagine that two strengthened layers coalesce when h_0 is very low, so that f increases. The hardening and crystallisation of a polymer in thin layers generally speaking lead to a different supermolecular structure and to a different distribution of residual stresses than in thick layers. Thus β and s in Eqn. (2) also vary with h_0.

A change in the thickness h_0 undoubtedly alters also the coefficient α. According to Eqns. (8) and (9), α for ideally plastic adhesive should be inversely proportional to the thickness h_0; however, there are no examples of such a relation in the literature. The effect of h_0 on f for viscoelastic materials (rubbers) should be very remarkable. Rubbers, like gases, offer little resistance to changes in shape but tend to retain a constant volume. If h_0 is small (see Fig. 9), an appreciable increase of h is impossible without a significant increase of the volume V, since the hollows visible at the end of the adhesive film cannot alter V appreciably. If S is the area of the end-face, then $dV \simeq Sdh$. On the other hand, when h_0 is large, the adherends can move far apart without altering V, as shown on the right-hand side of Fig. 9. Therefore one may expect that the increase of f with $1/h_0$ would be particularly pronounced for rubberlike adhesives.

The data for the effect of h_0 on the strength of lap joints are contradictory. The situation is somewhat clearer for the peeling resistance $\Gamma = F/w$. According to Eqn. (12), it is postulated that this resistance increases somewhat with the thickness h_0, i.e. the dependence of Γ on h_0 should be the opposite to that of f on h_0. A qualitative confirmation of this theoretical conclusion can be seen, for example, in the numerous measurements carried out by Gardon[63] on systems consisting of two cellophane ribbons glued together with polyacrylate. Thus, for a rate of rupture of 1 mm s^{-1}, Γ was approximately 100, 250, and 600 kdyn cm^{-1} for thicknesses h_0 of 1.2, 5.1, and 258 μm. According to elementary theory, Γ should have increased by a factor of 3.8 for an increase of h_0 by a factor of 215 (258 : 1.2 = 215); experiments showed that the increase was approximately by a factor of 6.

Since the mathematical theory of peeling and rupture is still very imperfect, one cannot expect a better agreement between theory and experiment. At any rate it is difficult to doubt that the dependence of f and Γ and h_0 has a purely mechanical origin and has nothing in common with molecular adhesion. It is very gratifying to note here that Berlin and Basin[10] essentially agree with this conclusion, which follows from experimental data and from the rheological theory of the strength of adhints.

Nevertheless the increase of the strength f with $1/h_0$ has been sometimes attributed[64] to molecular attraction.

It was suggested that both adherends in the adhesive joints attract one another through the intervening layer of adhesive and that this attraction is stronger the thinner the adhesive layer. This hypothesis was apparently initiated by Smilga and Deryagin[65]. If one nevertheless concludes that f varies with h_0 for mechanical reasons, one has to ask again the supporters of the molecular hypothesis what thickness h_0 corresponds to the equality of the measured strength to A. Some investigators believe that the extrapolation of f to $h_0 = 0$ would yield a value equal or close to A. In reality such extrapolation will affect most the coefficient β, which would then become approximately equal to unity; the experimental value of f will then be almost equal to the ratio $(\xi - s)/\alpha$.

3. The strength of the adhint and the adhesive. According to the rheological theory, the strength f of proper adhints is determined primarily by the strength of the adhesive f_M, since both in the rupture of both the adhint and of a free rod made of the adhesive the crack spreads in the same material. Nevertheless, in the general case f is not equal to f_M for reasons already described in section V. The equality $f = f_M$, can only occur, if it is not fortuitous, when the adhesive joint is made up in such a way that $\alpha = 1$, when the local stress concentrations β are equal in both systems, and when the heat-treatment temperature (and other external conditions) have been chosen so that the stress s_M in the free adhesive differs little from s in the adhint. When all these factors are taken into account in the formation of adhesive joints, the equality of f (for a large thickness of the adhesive layer) and f_M can be demonstrated experimentally, as shown in Fig. 7. In the majority of experiments carried out to compare f with f_M, the values of α, β, and f were not taken into considerations, so that an exact equality of f and f_M cannot be expected. Nevertheless, there is no doubt about a close relation between these two strengths even when the above experiments are considered.

Resistance to rupture f of butt joints and the strength of free adhesive f_M (in bars).

Adhesive	Adherend			f_M	f/f_M
	steel	copper	aluminium		
	f				
Polyamide 6	720	730	660	830	0.84
Polyamide 66	680	750	670	720	0.97
Polyamide 610	530	620	570	480	1.18
Polyamide 11	390	260	410	590	0.60
Polyethylene	170	110	170	300	0.50

The Table compares the values of f and f_M for five adhesives and three adherends; adhesive pin-type butt joints were employed.

The first column indicates the composition of the adhesive, the next three give the values of f, the fifth column lists the f_M, and the sixth gives the ratio of the average values of f and f_M. Polyethylene was not specially purified, since its low f/f_M ratio probably indicates the presence of a weak boundary layer. Nothing is known about the purity of polyamide 11. The f/f_M ratio for other polyamides is so close to unity that there is no doubt about the mechanism of rupture. It is remarkable that f for adhesive joints between two copper "pins" (third column) differed appreciably from the f (was smaller) for other metals only in the case of the two adhesives where the low ratio f/f_M suggests that contaminants may be present in the interfacial layer. It may be that copper accelerates the oxidation of adhesives, as mentioned in section III, 7. In systems for which f was almost equal to f_M, f was independent of the nature of the metal: the average f was 640 bars for steel, 700 bars for copper, and 630 bars for aluminium. From the standpoint of the rheological theory, this result is obvious: since the mechanical properties of different adherends differ, it follows that the coefficients α in their adhints also depend on the nature of the adherend; but when the α nevertheless differ little from unity (as in the systems of Lewis and Tanner), the differences between three similar values of α hardly affect the resistance to stripping. It is difficult to account for the independence of f of the nature of the adherend in terms of the molecular theory; it is difficult to believe that the molecular adhesion of a polymer remains constant whatever the change in the oxide to which the polymer is attached.

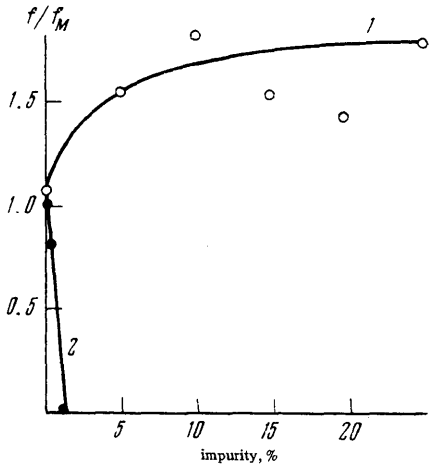


Figure 15. Difference between proper (upper curve) and improper (lower curve) adhints. Abscissa—percentage of contaminant. Ordinate—f/f_M ratio: 1) ethyl palmitate; 2) oleic acid; both in purified polyethylene.

The similarity or even equality of two values of f and f_M, which cannot be accounted for on the basis of the molecular hypothesis, has been noted many times in the literature. Some data have already been presented in section VI, 1 and VI, 2. As early as 1932, Nightingale[67] concluded on the basis of numerous observations that the strength of the soldered joints and the solder differ little however the chemical composition of the solder is varied. The resistance to rupture f in a system of two quartz cylinders with an intervening layer of solid paraffin increased from 3.3 to 14.6 bars when the thickness of the adhesive layer was diminished from 2.5 to 0.003 mm, while the tensile strength of the paraffin was 7.3 bars[68]; it may be that α in the thick adhints was 7.3 : 3.3. The f/f_M ratio varied only in the range 0.62 — 0.70 when four different adhesives consisting of an epoxy-resin cross-linked with diethylenetriamine were ruptured in the form of three bars or in the

form of layers between two aluminium cylinders. The tensile strength of ice between 0° and −10°C usually varies between 10 and 18 bars and butt joints in which copper, steel, and glass adherends were joined by a film of ice broke[69] following the application of a stress of 19 bars.

All these quantitative agreements between f and f_M are observed only because the adhesive joints are of the proper type (see section V). Fig. 15 presents certain data[15] clearly demonstrating the difference between proper and improper adhints. In Fig. 15 the fraction f/f_M is plotted against the weight ratio of the impurity (in purified polyethylene) relative to the overall weight, so that 0.05 on the abscissa axis represents a mixture comprising 0.05 g of the impurity and 0.95 g of polyethylene. The adherends consisted of stainless steel and the shape was such that α in the system was only slightly higher than unity. Curve *1* refers to mixtures of purified polyethylene and ethyl palmitate. Evidently f exceeded f_M at all impurity concentrations; one must suppose that this phenomenon was due to the factor β: on addition of palmitate, polyethylene became softened to such an extent that it was difficult to prepare from it well-formed bars for the measurement f_M. Curve *2* has been plotted for mixtures of purified polyethylene and oleic acid; here f/f_M decreases almost to zero when the concentration of the impurity is only 1%. The difference between the two curves is striking; it corresponds to a profound difference between proper (ethyl palmitate) and improper (oleic acid) adhints. The resistance to rupture of improper adhints has nothing in common with the strength of the adhesive and is much lower than the latter, since rupture does not occur in the adhesive but in a weak boundary layer.

4. The strength of adhints and the composition of the adhesive. The difference between the rheological and molecular theories of strength is shown perhaps most clearly in an examination of the dependence of strength on the molecular composition and structure of the adhesive. Unfortunately this difference remains qualitative in principle because the predictions of the molecular hypothesis are so nebulous that no quantitative or even semiquantitative conclusions can be derived from it. After repeated attempts to provide the molecular hypothesis with flesh and bones, one must conclude that essentially this theory does not exist; there are only feelings, emotions, and guesses.

What sort of theory could it be? It could relate f, for example, to the densities of cohesion energy ($\lambda\rho$) or to solubility parameters ($\sqrt{\lambda\rho}$); λ denotes the latent heat of evaporation per gramme and ρ the density (g cm^{-3}); the dimensions of the product $\lambda\rho$ are g cm^{-1} s^{-2}, i.e. the same as those of the stress. We shall designate the adhesive by the numeral 1 and the adherend by 2; then one of the possible rules of the molecular theory would be represented by the expression $f = \lambda_1\rho_1 - k(\lambda_2\rho_2 - \lambda_1\rho_1)$, where k is an unknown constant. According to this formula, when the adherend and the adhesive are very similar, $f = \lambda_1\rho_1$ and f is smaller the smaller the difference between $\lambda_1\rho_1$ and $\lambda_2\rho_2$. This rule resembles the empirical rules for the miscibility of liquids. Or f might obey the "rule of polarities": $f = a - b|n_2\mu_2 - n_1\mu_1|$, where a and b are two unknown constants, n_1 and n_2 are the numbers of dipoles per unit volume of the adhesive and the adherend, and μ_1 and μ_2 are their molecular dipole moments. When $n_2\mu_2 \simeq n_1\mu_1$, i.e. the adhesive and the adherend are both polar or both non-polar, f reaches the maximum possible value (a); if the difference $|n_2\mu_2 - n_1\mu_1|$ is large, f is much lower than a.

No rule of this kind appears to be quoted in the literature. In the formulation of the "rule of polarities" no one has even explained what meaning should be assigned to polarity: the dipole moment of the chemical bond (for example C—H), or the permanent dipole moment μ of an individual molecule (according to this criterion, even toluene is polar), or the product $n\mu$ just employed, or some other quantity. Incidentally, one cannot avoid a conflict between the "rule of polarities", however defined, and facts: non-polar polyethylene can be very effectively glued to glass and metals, while ethyl palmitate and oleic acid (the dipole moments of which are identical) have different effects on f for polyethylene adhints.

According to the rheological theory, which alone can claim to have a general significance and which alone is capable of quantitative predictions, the composition and structure of the adhesive influence the strength of the adhint via two completely different mechanisms depending on whether the proper adhint ⇌ improper adhint transition is observed. As already stated, the mechanisms of the formation of weak boundary layers are extremely varied and a change in the composition of the adhesive can readily include or exclude one of these mechanisms.

For example, we shall suppose that the chemical composition of the adhesive varies systematically in such a way that the surface tension γ of the liquid adhesive increases continuously. Since the contact angle θ usually increases with γ, at some point in the series, i.e. for a particular composition of the adhesive, the wetting will become insufficient and it will be impossible to remove air bubbles from the surface of the adherend with the liquid adhesive. In this series all the initial members (for which γ is low) will give rise to proper adhints (with high values of f), while the adhints formed by all subsequent members will break on application of weak stresses f in a weak boundary layer of the first kind.

A change in the chemical nature of the adhesive can lead to weak boundary layers of the first group, which are independent of contact angles. We shall examine a series of polymers with similar structures but with a gradually increasing molecular weight M. In many cases, when M increases, the melting point and the viscosity of the melt also increase. If the conditions governing the formation of the adhint are maintained strictly constant, for example, when the system is heated for a specific time at a specific temperature, the duration of heating may be sufficient for the removal of air bubbles when M of the liquid is low but may be too short for very viscous liquids with high molecular weights. Possibly, this is the cause (or one of the causes) of the observation that the strength of adhesive joints is sometimes a maximum for a moderate value of M of the adhesive; for example, epoxy-resins cross-linked with triethanolammonium titanate gives rise to the maximum f (shear resistance) for M = 800.

It would be easy to test this explanation. It would be necessary to measure the tensile strength f_M of the same polymers in the form of free rods and compare it with f. If f is similar to f_M for all $M < 800$ and much lower than f_M for $M > 800$, then the presence of a weak boundary layer in the second group of specimens would be very probable. Unfortunately f_M has not been measured and compared with f. This is an example of an extremely common error, which frequently lowers the level of experiments from scientific to empirical. Those who wish to understand the mechanism of the phenomenon, find the measurement of the tensile strength of adhesive joints almost useless if they are not supplemented at least by data concerning the dimensions of the specimen and the

measurements of f_M and of the thickness of the residual adhesive on the adherend. Well-founded conclusions concerning the mechanism can be reached only if the geometry of the system, the location of rupture, and the degree of similarity between f and f_M are known.

By altering the chemical nature of the adhesive, it is possible to pass from proper to improper adhints of the second group, described in section III, 2. If a liquid X is soluble in a solid adhesive A up to a concentration c_0(%), then the adhesive joints in which the adhesive has the composition $(100 - c)A + cX$ have a high strength f as long as $c < c_0$ but disintegrate readily exactly along the interface when $c > c_0$. As already stated, transitions of this kind were observed on dissolution of oleic acid in purified polyethylene. Probably they occurred also in a system comprising an epoxy-resin and tetraethylenepentamine (TEPA).[70] Butt joints between copper "pins" had a tensile strength of about 700 bars when c of the amine was 5 — 9%. When the TEPA concentration was raised to 17%, f fell approximately to 80 bars; at the same time the location of rupture migrated from the bulk of the adhesive to the interface. The strength f_M of free films of the same polymer was somewhat less than 600 bars for a ratio TEPA: epoxy-resin = 0.08 and depended little on it following further cross-linking; thus the ratio of the two strengths f/f_M was approximately 1.2 for c = 7%, 0.17 for c = 17%, and 0.07 for c = 0.33%. The curve obtained at high concentrations resembles the f/f_M curve for mixtures of polyethylene and oleic acid illustrated in Fig. 15. Probably the excess tetraethylenepentamine formed a weak boundary layer in which rupture in fact occurred. It is noteworthy that in the above investigation measurements were made of f_M and the location of rupture was determined at least qualitatively; therefore the mechanism of failure can be actually inferred and not merely discussed.

In other cases one must employ as a basis only the values of the strength and not the author's impression that the rupture was cohesional or adhesional. Films of synthetic and natural rubber were peeled from cellophane freed from glycerol[71]. The peeling resistance Γ was on average 1400 kdyn cm^{-1} for synthetic rubber and only 18 kdyn cm^{-1} for natural rubber. This difference cannot be reduced to a difference between the mechanical properties of the polymers; natural rubber, the peeling of which was "adhesional", undoubtedly formed a weak boundary layer at the junction with cellophane and probably also at the junction with other polymers[72]. Unfortunately it was impossible to find any data concerning the nature of this layer. Only on peeling natural rubber from polyisobutylene, did Γ exceed 300 kdyn cm^{-1}; one must suppose that the material of the weak boundary layer formed by natural rubber dissolved in polyisobutylene, which is very similar chemically to natural rubber. Γ for polymeric coatings on ordinary polyethylene was also very low with the exception of two butadiene rubbers; is it possible that neutral impurities present in polyethylene are soluble in polybutadienes?

Weak boundary layers of the fixed kind, formed in chemical reactions between an adhesive and an adherend, can also arise and disappear as the composition of the adhesive is varied systematically. In Berlin and Basin's book[10], where the molecular hypothesis of strength is defended, it is mentioned that the introduction of maleic acid into copolymers of vinyl chloride and vinyl acetate increases their "adhesion to metals" (i.e. f), but at the same time it accelerates corrosion and is therefore impractical. It is indeed remarkable how truth driven out of the door returns through the window; where else would one expect to find strong adhesion if not between an acid and a metal!

Possibly the TEPA — epoxy-resin system mentioned above is an example of improper adhints of the sixth and not the second kind. The point is that f for adhesive joints between titanium "pins" did not fall below 500 bar even when the ratio TEPA : resins was 0.25. One must suppose that the excess TEPA did not form weak boundary layers by itself but together with copper, which readily enters into complexes with amines. Additional examples are presented in section III, 6.

In those very numerous systems where no proper adhints $\rightleftharpoons$ improper adhints transitions occur and all the adhesive joints may be regarded as proper, the effect of composition on f and Γ may be elucidated on the basis of Eqns. (2) and (12).

According to Eqn. (12), Γ is proportional to the strength f_M. In Eqn. (2), the ratio ξ/β is close to f_M although the coefficient β is usually smaller in a thin "fillet" of adhesive than in a large bar employed for the measurement of f_M. Perhaps one may expect that both f and Γ will increase with the strength f_M of the free adhesive. This prediction of the rheological theory is fairly frequently confirmed. The variation of f and Γ with f_M is so evident that it cannot fail to be noted even by convinced supporters of the molecular hypothesis; thus one group of investigators[73] admit that the "problem of adhesional strength is inseparable... from the problem of cohesional strength"; and others[30] attribute the impairment of the "adhesive capacity" of polymeric esters (on increasing the length of the alkyl group) to the "decrease of the cohesional strength of polymers". Thus the chemical composition of a solid determines to a large extent the value of f_M and to a somewhat lesser extent also f and Γ. To a lesser extent partly because β in the adhesive layer can differ markedly from β_M in a free adhesive specimen. It is quite likely that the evaporation of the solvent from the free specimen will take place without hindrance, while evaporation from a film between two adherends will be so difficult that β_M will prove to be several times smaller than β. Since the strength of solids is equal to the strength of their weakest section, it is insufficient to state (and to note) that a substance A served as the adhesive. How was it prepared? What kind of defects remained in it? In order to understand the results of experiments on adhesive joints, it is almost necessary to have bacteriological information about them. Just as to the bacteriologist a gel containing one part by weight of tubercle bacilli per 10^{12} parts of agar is quite unlike the gel from which Koch bacilli are absent, to the investigator of strength a cubic centimetre of a solid in which a cubic micron contains a sharp crack differs decisively from another cubic centimetre in which such cracks are absent.

The composition of the adhesive can have different effects on the stripping resistance f and on f_M also because the coefficient α varies with composition. Generally speaking, α is higher the greater the difference $E - E_1$ or the ratio E/E_1; we may recall that E is the modulus of elasticity of the adherend and E_1 that of the adhesive. By varying the chemical nature of the adhesive, we also alter its E_1. Certain strength curves with a maximum may be obtained because $E = E_1$ and $\alpha = 1$ when the composition corresponds to the maximum. For example, we may suppose that two rubber "pins" are glued together with a rubber adhesive and that the composition of the adhesive is varied systematically by the introduction of increasing amounts of chlorine into the rubber. The stripping resistance f in this system may initially increase because E_1

increases with the amount of chlorine and $E - E_1$ decreases; at a certain chlorine concentration, $E_1 = E$ and f reaches its maximum value; on further introduction of chlorine, E_1 becomes greater than E, α again increases, and f again diminishes. This explanation too could be easily tested; it would be sufficient to replace rubber adherends by glass or steel adherends for which E would remain in all cases much higher than E_1; in such systems a maximum would not be observed. As a result of an incorrect hypothesis, such comparison has not been made.

The difference between the residual stresses s has already been resorted to frequently for the explanation of the incomplete agreement between the effect of composition on f and f_M. The relaxation of stresses in a free bar of adhesive takes place in many cases more readily and more completely than in a "fillet" clamped between two rigid adherends; consequently the quantity $\zeta/\beta - s$ in the bar is frequently higher than in the layer of adhesive.

In an examination of butt joints, it is usually permissible to assume that the adherends are completely undeformed during the rupture process. Such an assumption is rarely justified for lap joints and never for peeling and rupture. In such systems the values of f and Γ have no physical significance if the reader is not informed about the dimensions and the mechanical properties of the adherends or if the experimenter did not pay attention to these factors.

The foregoing can be elucidated by the example quoted in the paper of Kardashev and Vakula[30]. A hydroxylated polyester was condensed with a mixture of tri-(*p*-isocyanatophenyl)methane (TIPM) $(OCN.C_6H_4)_3CH$ and hexamethylene di-isocyanate (HMDI) $[OCN(CH_2)_6NCO]$; the greater was the amount of TIPM in the mixture, the denser was the cross-linking between the chains formed by the polyester and HMDI and, one must suppose, the higher was the modulus E_1 of the polymer. This polymer has been used as an adhesive between two unknown adherends forming a lap joint. It was found that the shear resistance decreased monotonically with increase of the relative content of TIPM in the mixture. If the adherend consisted of plates, they were bent as shown in Fig. 12; it may be that peeling and not shear occurred. The peeling resistance is generally speaking lower the more rigid the adhesive; it is evident even from Eqn. (12), which under-estimates the influence of rigidity; Γ diminishes when E_1 increases. Consequently the effect of the concentration of TIPM on strength can be understood as follows: the greater the amount of TIPM, the higher E_1; the higher E_1, the lower Γ; and the quantity Γ and not the true shear resistance determined the strength of the lap joints. Again this explanation would not be difficult to test using massive bars instead of plates but the idea of such a test apparently did not occur to the authors.

All hypotheses relating the chemical structure of the adhesive directly to the values of f or Γ are incorrect, since they do not take into account the necessary values of α, β, s, f_M, etc. let alone the possibility of the proper adhint $\rightleftharpoons$ improper adhint transition. Moreover, they are arbitrary, since they are based on an arbitrary choice of certain chemical units and the neglect of all others. We may point to the simplest example taken from the paper of Kardashev and Vakula[30]. Adhesives containing RCH_3, RCH_2Cl and RCH_2Br molecules were compared. The conclusion arrived at as a result of the observations was that the "difference between the adhesive properties of halogen-containing polymers may be accounted for by the presence of bromine and chlorine atoms". How this can be explained is not unfortunately stated. Nor is it shown that the individual properties of the halogens are significant (for example, the structure of their electronic shells); it may be that the peeling resistance depended only on the molecular weight M of the adhesive and varied in the series RCH_3, RCH_2Cl, RCH_2Br exclusively because M also varied in this series.

A more complex example may be found in the paper by De Bruyne[74]. Lap joints were formed between aluminium plates with the aid of adhesives containing epoxy-resins and phthalic anhydride. All the polymers contained 0.85 of the molecule of the anhydride per epoxy-group but also present were n groups $[-OC_6H_4C(CH_3)_2-C_6H_4OCH_2CHOH.CH_2-]$, n being varied systematically from 0.05 to 5. The shear resistance was much greater for $n > 1.5$ than for $n < 0.5$. Since the tensile strength f_M of the free polymers (bars, films, etc.) usually increases with n, this observation can be most simply accounted for by the usual similarity between f and f_M. The author preferred to point out that with increase of n there is an increase in the number of hydroxy-groups in the adhesive and that therefore f is large when the concentration of hydroxyls is high. Evidently other conclusions just as valid are possible. The shear resistance f increases with the number of benzene rings; perhaps these rings are the cause of "adhesion". The presence of isopropylidene groups $(CH_3)_2C$: also increases f; it may be that "adhesion" is caused by them. The higher the value of n, the smaller the number of carboxy-groups (from phthalic anhydride); the carboxy-groups may suppress "adhesion". This last conclusion is particularly remarkable since supporters of the molecular hypothesis of strength usually assert that carboxy-groups promote "adhesion".

The word adhesion is not placed in quotes by the above investigators but in this review the quotes are necessary in order to remind the reader that the true molecular adhesion A has nothing in common with the resistance to stripping, shear, peeling, etc. Adhesion is not the only term employed improperly (see the remarks by Raevskii and Pritykin on this matter[75]). The terms "adhesive capacity" and "adhesive properties" are used. These properties do not exist. Any substance which can exist in the liquid or plastic state so that it can fill hollows on the surface of the adherend and is capable of solidification in contact with the adherend can serve as an adhesive.

There would be no need to quarrel about words, but the danger is that the expressions "adhesion of substance A to substance B" or the "adhesive capacity of A" lead the reader to the error according to which the resistance to rupture of a single arbitrary adhint is adopted as a constant and characteristic property of the substance. Thus the resistance to rupture of films of a polyethylene and of P-118 polyisobutylene was found to be 95 kdyn cm^{-1} when the films had a particular thickness, a particular width, contained particular impurities, etc.; this resistance would be different if the amounts and nature of the impurities, the width, the thickness, etc. were altered; therefore the assertion that the "adhesion" of polybutylene to polyethylene is 95 kdyn cm^{-1} is illogical.

The main reason for the popularity of erroneous views is that organic chemists, who, of course, synthesise polymeric adhesives, continue to work on them in the field of tests and applications. Specialists in the measurement of strength and other mechanical properties of materials must be induced to undertake critical tests of the strength of adhesive joints. Since generally speaking organic chemists are unfamiliar with the science of the resistance of materials, the theory of elasticity, etc., they do not

find the evidence based on these sciences to be convincing. It is very remarkable that Berlin and Basin[10] mention the work on polyethylene briefly described in section III, 2 of the present review in a section devoted to the "morphology of the solid surface" (Ref. 10, p. 56) although polyethylene is an adhesive and not an adherend; in the description of the use of polyethylene as an adhesive on pages 196 and 197 of Ref. 10, it is written that "evidently the appearance of oxygen-containing groups in polyethylene... is the main cause" of the increase of the strength polyethylene adhints when polyethylenes are subjected to a special treatment. As mentioned in section III, 2 (and of course in the papers describing the original experiments), all the adhesive joints were formed in an atmosphere of nitrogen and the purified polyethylene contained less oxygen than the initial material.

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