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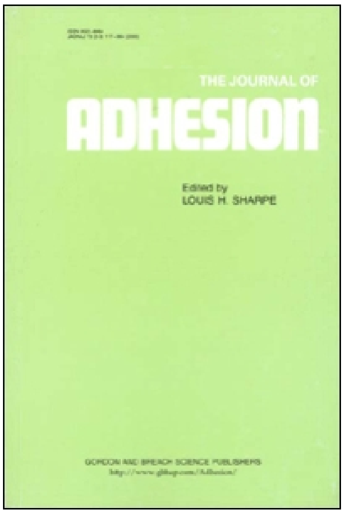

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Some Aspects of the Theory of Adhesive Joints

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The molecular and the rheological theories of adhesion are compared and the limits of their applicability discussed.

The theory of adhesive joints was a subject of discussion for many decennia but there is still no unanimity even in respect to most fundamental notions. Something like 10 ideas are discussed or separately developed, more than 40 definitions of adhesion have been proposed,[1] and the very possibility of a single theory of the phenomenon is denied.[2] Criticism of the newly developed ideas[5,6] by the proponents[3,4] of "old" theories deals with basic problems. The disarray of these notions resulted in a very recent attempt[7,8] to modify the rheological theory initiated and developed by Bikerman.[6,9]

The absence of any agreement on the basic aspects of the theory of adhesive joints renders their further discussion necessary, although the problem may appear trivial.

The first conclusion of the lengthy discussions on the nature of adhesion and the strength of adhesive joints, if these are understood as any assemblies obtained by non-mechanical fastening, is that a single general theory of the phenomenon is possible; the overwhelming majority of the scholars agrees with this conclusion. As instances of such a theory, the molecular theory[11] which combines ideas of several authors, and the original theory of Bikerman[6,9,12] named "rheological" by him may be referred to. These two systems include the diffusion,[13] the electric,[14] the microrheological,[15] the electrorelaxation,[16] the chemical,[17] the adsorption,[18] and the mechanical[19] hypotheses which still are classified as theories of adhesion although in reality they deal only with special instances of the mechanism of adhesion and are valid only for a narrow field of objects brought into mutual contact at given circumstances.[20]†

The aim of this paper is to consider the existing alternatives in the hope of more clearly defining their advantages and their application limits.

I COMPARISON OF THE BASIC IDEAS OF THE RHEOLOGICAL AND THE MOLECULAR THEORIES

According to the molecular theory, the strength of adhesive joints is determined by the magnitude of the specific adhesion energy, whose notion was introduced in,[23] that is, the specific energy of attractions which arise along the geometric phase boundary of adhesive and adherend on their molecular contact. According to the rheological theory, this strength is independent of the specific adhesion energy and is determined only by the cohesional strength of the weakest element of the joint. This element is the weak boundary layer in "improper" and the adhesive (or the adherend) in "proper" joints.[9,12]

These two theories are fundamentally different not only as far as their postulates and proofs are concerned, but also in the practical advices for achieving joints of high strength and duration. An investigator relying on the molecular theory would formulate or synthesize an adhesive which guarantees the highest energy of attraction to the given adherend. Because of this tendency, over ten thousand adhesive compositions are known to the international industry, and their number continues to increase. The rheological theory considers all these efforts totally wasted and directs the investigator to a search of conditions guaranteeing formation of "proper" joints and a high cohesional strength of the adhesive. It inspired numerous publications on the formation technology of joints and on the means of elimination of weak boundary layers. In order to compare the two theories and to delineate their areas of application, it is necessary first of all to elucidate the basic notions.

Adhesive joints may be considered either from the viewpoint of their preparation or of their utilization. In the first instance, a theory of formation, and in the second, a theory of strength is needed.

Formation of an adhesive joint consists of two independent consecutives stages, namely a macroprocess of establishment and growth of the area of molecular contact between adhesive and adherend because of wetting and

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† Analogous ideas developed for non-polymers include the theories of metal seizure[21] and of the adhesion of finely dispersed solids.[22]

flow, and a microprocess of attractive interaction (at molecular contact) whose mechanism is related to sorption. The advocates of both theories would agree with this description. However, the rheological theory has no need for the second stage as this does not affect the strength of the joints (according to the theory). On the other hand, the molecular theory deals only with the second stage and is not applicable to the first as no theory of molecular interaction along the interface of two phases should and can describe volume processes of reversible or irreversible phase deformations. These attitudes of the two theories are reflected also in their designations. It seems that the root of the contradictions between them lies in the difference between the phenomena on which the attention is focussed.

The objection to this treatment is that the two stages are contrasted or one of them is ignored, while both ought to be considered in the framework of a single, actually existing two-stage process. This misunderstanding caused the well-known disputation concerning the effect of wetting on the strength of adhesive joints, in which some authors[5] demonstrated the importance of wetting in the formation processes of joints, while their opponents[3] negated any correlation between strength and wetting on the basis of the fact that wetting did not affect adhesion. It is clear that no discussion can be productive at these divergent approaches.

Simple physico-chemical[27] and thermodynamic[28] reasonings and also consideration of the probability of the direction of crack growth during rupture of adhesive joints[8,9] permit us to believe that the energy of interfacial interaction always exceeds the cohesion energy of the weaker phase[8,9] and that the probability of crack growth along the geometric contact boundary is immeasurably smaller than that of a rupture within a phase. Although this statement in our opinion requires clarification, it needs no detailed discussion in this section, because it is accepted by both the rheological[8,9] and the molecular[11,29,30] theories.

Moreover, the rheological theory starts from this statement, whereas the molecular theory attempts to derive it by confirming that the van-der-Waals forces alone are sufficient to assure the cohesional type of rupture.[30] By accepting this conclusion, the proponents of the molecular theory must, of necessity, accept also the general validity of the above statement.† The necessity of cohesional failure causes the strength of adhesive joints to be independent of the magnitude of adhesion. Consequently, the strength of joints is determined only by the degree of completion of the molecular contact. Thus, the molecular theory which deals with interactions along

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† In this connection, the most recent paper[7] of the authors of references [11,30] appears strange; in it they combat the idea[6,9] of the necessity of cohesional rupture. It may be added that these authors committed similar contradictions also in earlier publications.[11,31]

interface boundaries in principle cannot be utilized to account for the joint strength, and the rheological theory remains the only correct theory which indicates the quantities responsible for the strength of joints. From the above it follows also that Bikerman,[6,9] contrary to the advocates of the molecular theory, is right in maintaining that measurements of joint strength supply no information on adhesion interaction.

However, it should be kept in mind that rupture in cohesion is prescribed and encountered only because, along the phase boundary, attractive interactions are present whose energy exceeds the cohesional energies in the phase volumes. The presence of attractions at molecular contact of two phases necessitates a term which would characterize both the conditions of formation and the consequences of the attractions. *Adhesion* is this term. It should be defined as a surface effect consisting in the emergence of a physical (or also a chemical) attraction between the molecules (or ions) on the surfaces of the condensed phases at their mutual contact, which attraction leads to the union of these surfaces.[1] This definition treats adhesion as a universal physico-chemical (rather than technological) phenomenon, classifies it as a surface effect, characterizes it over the whole spectrum of attraction energies, points out the conditions of its technical utilization (that is, the presence of molecular contact) and the possible substrates (that is, any condensed phase independently of its nature and structure), and, finally, defines the end result as formation of a real physical system (that is, an adhesive joint).†

It follows then that the notions of "adhesion" and "the strength of adhesive joints" are not at all equivalent either quantitatively or qualitatively. Although this statement is obvious, it is very rarely pointed out[33] by the partisans of the "old" and the molecular theories of adhesion[7,11,13,14–16,18,19 22,29,30,31] although it is never doubted by the specialists in the strength of adhesive joints.[34]

II DEVELOPMENT OF THE THEORY OF ADHESIVE JOINTS

It is clear from the above that, when the problem of adhesive joints is considered, three independent notions are used, namely adhesion (as a phenomenon), formation of a joint (as a combination of processes), and its strength (as a property of the joint). This property is determined not only by the conditions of testing and use but also by the geometry of the joint.

Because the above concepts are mutually independent, it is necessary to

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† Presumably, adhesion as a phenomenon is encountered not only in sticking with formation of adhesive joints but is basic also for friction and adsorption.

approach each of them separately and to construct theories for every one.† Consequently, the molecular theory may serve as a base for creating an adhesion theory of condensed phases if it restricts itself to the problems related to the phase interaction along their contact and ceases to be applied to formation processes of this contact and, above all, to the strength of adhesive joints.

The above problems are important for the sorption of high molecular compounds from melts and concentrated solutions and also for the sorption of oligomers and liquid monomers by solid surfaces. These processes in many instances are associated with diffusion (in volume, near interface, or in the interface), polymerization, and other processes which markedly complicate the mechanism and the kinetics of sorption.

The theory of adhesion should start by accepting the two-stage process of achieving the adhesion equilibrium, namely sorption of the initial adhesive (melt, solution, monomer, or oligomer) having particular kinetics and characteristics, and alteration of adsorptive interactions and the structure of the layer near the surface, due to transformation of the adhesive into its final state (cooling of the melt, removal of the solvent, polymerization).

The rheological theory should describe only the macro-processes of the formation of molecular contact without referring to the micro-processes of interfacial interaction and to the problems of the strength of adhesive joints, that is, it should be restricted to the questions of wetting, spontaneous or forced flow of thin films and interfacial layers, capillary filling, etc. Its task is finding quantitative relations between the rate of growth of molecular contact area and the properties of the adhesive, the surface characteristics of the adherend, and the schedule of the formation process. Good (although special) instances of such an approach are given in references.[35,36]

The theory of strength of adhesive joints should deal only with the nature of strength and rupture on the basis of the general rules of the cohesional strength of polymers and should not refer to the mechanism and rate of the joint formation and to the interactions along the phase boundary. An independent chapter based on this theory would treat the design of adhesive joints to which so far practically no attention was given.

III SOME PECULIARITIES OF TECHNICAL ADHESIVE JOINTS

In the actual formaton and use of adhesive joints, the interaction between the adhesive (A) and the adherend (B) is not confined to the attraction of

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† Analogously, there is no general theory of a material; only a theory of its synthesis, utilization, and strength exists; it is the subject of the materials science and supplies full information on a given material. When also the construction (in which the material is used) is known, the information on the behavior of the material is complete.

their surfaces. Because of various physical and chemical processes occurring on the surfaces of the initial materials before their joining, and on the interface later, adhesive joints contain intermediate layers (C) whose detailed classification is given in reference [12]. In principle, their presence excludes molecular contact between A and B so that it makes no physical sense to speak of an adhesion of A to B. The presence of these layers may cause rupture of the joint in phase C whenever this has a smaller cohesive strength than the adhesive and the adherend. Consequently, in the praxis of joining, efforts should be directed to detecting weak boundary layers possible in given composition and conditions, and to designing such formation conditions that phase C is excluded or that the "weak" boundary layer is strengthened by, for instance, altering its structure.

In this connection, devices employed by the partisans of the molecular theory of adhesion[11] and of the diffusion theory[13] may be useful insofar as they result in the removal or strengthening of weak boundary layers. From this viewpoint, mutual diffusion is not useless as claimed[37] and not necessarily bad as follows from the instances mentioned in a paper[9] in which instances the diffusion is associated with pore and void formation in the contact zone. In the materials for which the diffusion theory was developed[13] (i.e., polymers in viscous or viscoelastic state), no pore or void formation in the contact zone is observed because of the great mobility of the segments of macromolecules. In these instances, all devices employed for intensifying diffusion processes surely are useful since they always facilitate the dissolution of "weak" boundary layers. Analogous statements are valid also for chemical bonds across the phase interface. The bonds may be disadvantageous[6,9] if they cause corrosion and formation of "weak" boundary layers, i.e., transform "proper" into "improper" joints, but they certainly are useful if they result in strengthening of the above layers.

The above considerations apply to adhesive joints which, in use, are not subjected to high temperatures, corrosive media, and, above all, solvents. When these agents act, formation of chemical links becomes equally necessary in the volume of the adhesive and along the interface of the phases, analogously to the advantage of links generally accepted for heat-resistant and solvent-resistant polymeric materials. In other words, if intermolecular forces cannot exclude flow processes (at high temperatures) or dissolution in solvents (of a material or an adhesive joint), the advantages of a chemical cross-linking are generally recognised and this is widely employed. This principle fully applies to adhesive joints, including the interaction zone of the two phases.

As far as polymer adhesives are concerned, their chemical reaction with the adherend may be useful also when the joints are used in normal conditions. It is known from the work by Zhurkov[38] on solid polymers and by

Gul[39] on high-elastic polymers that rupture of high-molecular, in contradistinction to low-molecular compounds, is always associated with breaking-up of molecules. This is caused by the existence of knots and by the excess of the total energy of intermolecular interaction along the chain over the energy of intramolecular chemical bonds. When an adhesive joint ruptures in the adhesive, this rule is still correct. When the rupture is in adhesion, i.e., the adhesive is separated from the adherend, splitting of molecules is not always necessary.

In fact, although the energy of a single act of molecular interaction between the phases A and B is greater than that in the volumes of A and B, the density of adsorption interactions may be less than that in the phase because of the limited number of active centers on the surface of the adherend. Consequently the specific adhesion energy may be smaller than the specific cohesion energy; in this instance, separation of the adhesive molecules without their splitting becomes possible. Moreover, according to the modern data,[40] orientation of adhesive molecules along the adherend surface has a small probability. A macromolecule touches the adherend surface in a limited number of points only, and the combined energy of these contacts may be smaller than, or equal to, the energy of the chemical bond in the molecule. This also facilitates separation of the molecule without splitting it.

The experimental methods of determining specific cohesion energy do not take account of the above situation because they are based on dissolution phenomena, that is, on a consequent (rather than simultaneous) rupture of molecular bonds along the chain, and disregard the energy of rupture of chemical bonds. Consequently, the measurable magnitude of specific cohesion energy may be smaller than the energy of mechanical destruction of polymers.

Analogously, to determine the rupture mechanism of adhesive joints, it is not permissible to use the comparisons, developed for low-molecular substances, between specific cohesion and interphase energies, as was done in the recent review by Bikerman.[9] Unfortunately, this objection against one of Bikerman's postulates remained unanswered although it was voiced long ago.[4] In our opinion, this postulate requires further discussion, whereas the validity of the other statements in Bikerman's theory is obvious and needs no additional proofs.

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