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Gaps between Theory and Practice of Adhesion†

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Diagnosis of many future adhesion problems will be based on current knowledge, reported at this symposium. But, *prognosis* permitting a decisive choice of materials and of methods in a specific situation, is not always possible. Considering the broad range of disciplines involved, a systems approach is proposed to reach a logical overlap between theory and practice. Four systems will be discussed in some detail.

The established concepts of adhesive strength in *mechanical systems* should be amended by a consideration of fracture energies in terms of a macroscopic, continuum model, followed by a discussion of microscopic and molecular structures. *Interface systems* are common to both adhesion science and tribology. Recent work on the nature of static friction and of boundary lubrication has contributed to the understanding of interface adhesion. Among the operational variables evaluated in *production systems* the "adhesionable" properties of adherends are badly in need of closer examination. In *biological systems* the strength and toughness of calciferous tissues should be compared with the corresponding properties of interlocking adhesives.

INTRODUCTION

Contemporary knowledge of adhesion, and of open problems, was reviewed some time ago¹. Recently emphasis has shifted slightly from the physics to the chemistry of adhesion, as will be evident from advances reported at the first and second session of this symposium. Polymer science, its terminology and techniques, has become an integral part of adhesion science, therefore it figures prominently in contributions to most of the sessions. Some current problems, regarding the treatment of adherends or the choice of adhesives,

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can now be subjected to a comprehensive analysis, culminating in diagnosis of unexpected failures and followed by prognosis of parameters, critical in future developments; this can be done indeed, at least on a laboratory scale.

A bird's eye view of applications is more difficult to produce; an early attempt to link science and adhesion technology² made only 'staccato' reading. In fact, Session six here covers but a few aspects of adhesion engineering. Problems can stem from many fields, ranging from aerospace to architecture or from selenology³ to surgery. To-day's students are taught the use of *Dynamic Systems* inter alia in the analysis of electrical, mechanical or production problems⁴. In future, therefore, one might expect an appropriate network model presentation of the ubiquitous adhesion phenomena and their interacting parameters. Decisions in technology depend more on behavioural and economical criteria² than on scientific arguments, as the limitations of empirical laws are not always recognized in time. So-called well-established engineering rules, if applied to new and yet little explored fields, can lead to major disappointments⁵, some of which are relevant to the present discussion.

Any technical adhesion problem is linked at one point or another with THE WORLD OF THE MECHANICAL ENGINEER. The subjects treated at this symposium are, in part, familiar to engineers, but engineers arrange concepts in an order differing from that used by chemists. The recent classification of subjects given in Applied Mechanics Reviews⁶ is the result of twenty-five years' evolution and has international approval. In it THE SURFACE has no place of its own. Here, *rheology*, "a science devoted to the study of deformation and flow of matter"⁷, is restricted to the "mechanics of fluids", while *viscoelasticity* is placed between the elastic and plastic properties of solids. Such differences in outlook must be recognized in order to ease the flow of knowledge, the more so as mechanical engineers have contributed so much to the science of metallic adhesion.

The design of machine elements for space vehicles led to studies of adhesion in an ultra-high vacuum (uhv)^{8,9}. New techniques resulted which were suitable for exploring the mechanisms of interaction of clean metallic surfaces. Adhesion here is identical with *static friction*, the next step then, the onset of dynamic friction, leads to another branch of mechanical engineering, *tribology* defined as: "the science and technology of interacting surfaces in relative motion and of the practices related thereto"¹⁰. Tribology and "the science and technology of adhesion processes" (actually a single term is badly needed) are both concerned with "interacting surfaces", thus these fields have many of their complexities in common.

Among the potential users of this symposium volume might be an aerospace designer, a metallurgist, a production engineer and a surgeon. Some of their specific adhesion problems will be outlined in the following discussion.

MECHANICAL SYSTEMS AND THE DESIGNER

Materials and models

Trained in the use of conventional materials—bricks, concrete, timber and metals—but confronted with new products, a designer will demand data fitting into his “formulae of stress and strain”. Neither potentialities nor limitations of carbon-black filled rubbers, fibre reinforced plastics, bonded metals, in fact a plethora of composite materials, can be assessed by this approach. Considerable re-thinking was needed to define design limits of ‘tough’ or ‘strong’ or ‘light weight’ new materials¹¹. Accordingly new tests and new test pieces were developed, serving as models, in the interpretation of certain mechanical properties in terms of the continuum theory of matter. Early promise¹² and *intrinsic* limitations¹³ were discussed at two meetings of the Royal Society, held seven years apart^{12,13}. Engineering needs are covered by a continual series of ASTM monographs.¹⁴

The prognostic value of this macroscopic approach is limited by the failing of the *principle of geometrical similarity* near the interface or interphase, in short near the glue line. In a complex and highly anisotropic medium shear strains cannot be properly defined. The conventional vectorial classification into *dilatational and deviatoric components* of strain becomes meaningless if the Poisson ratio of volume elements is inhomogeneous. While this has been recognized by some authors¹⁴, others¹³ try to avoid ambiguity by introducing such phenomenological terms as “interlaminar shear” and “fibre-matrix stress”. The nature of energy dissipation processes at interfaces is not yet properly understood and this lacuna further reduces the practical value of mechanical models.

In *mechanical fastening*, the viscoelastic (wood) or plastic (metal) properties of the components determine the strength of bonding; contributions made by adhesive forces are negligible. The pull-out process of a high modulus fibre embedded in a hard resin matrix, is presumably more like the removal of a long nail from concrete than that of shearing an adhesive bond. The so-called fibre-matrix “friction” depends on the bulk properties of the resin plus the presence of voids or of weak interlayers, rather than on interfacial adhesion. Some authors suggest that the adhesion of a tough plastic coating covering a micro-porous metal surface depends also on *mechanical interlocking*. Alternative experimental approaches are needed to distinguish between mechanical deformation energy and interface adhesion energy.

Only the timely arrival of the scanning electron microscope (SEM) has permitted *intuitive* interpretation of mechanical testing results, in terms of (sub)microscopical structures. The magnification of many a SEM analysis is well within the limits of conventional light microscopy, although of

course the three-dimensional perception reached with SEM pictures is unrivalled. Thus the diagnosis of adhesive strength and failure does not differ in principle from the interpretation of the earliest metallographic observations.

Modes of fracture

Even a seven-volume treatise¹⁵ cannot cover all aspects of fracture; there is now reasonable agreement on trends. The *fracture energy* concept has superseded the classical fracture force or ultimate strength theory. Evidence on local plastic deformation, preceding fracture, is derived from fracture markings, observed even with high modulus and apparently brittle materials. Knowledge about the size of these small volume elements and their ability to absorb deformation energy is essential for improving residual toughness in so-called brittle plastics. While the function of the rubber phase in impact-toughened plastics is fairly well-understood^{16,17} a corresponding study of nitrile rubber-phenolic or -epoxy resin blends (ref. 1, p. 75) is not yet available. Certain adhesive compositions fit the requirements of specification MM-A-132 for Mach-one (Type I) or Mach-three (Type IV) aircraft metal laminate (ref. 2, pp. 22-35). Obviously, the energy storage capacity under thermal stresses, needed in supersonic transport (SST) and space probe applications, will be closely related to fracture toughness and impact resistance of an adhesive at ambient temperature.

Mechanical testing experience has led to the formulation of safety limits for materials as far apart as fibreboard and bonded boron fibres. *Modes of failure*—cohesive, adhesive, interlaminar etc.—are defined and measured as part of the testing procedure. But, the adhesives formulator endeavours to identify the *cause* of failure in terms of material properties. Adhesive strength and failure (ref. 1, p. 100) is related to the mechanical deformation of adhesive and adherend; ultimate strength data yield little information on events occurring at the glue line. But, a discussion of the nucleation and growth of *voids* will permit a different classification of failure criteria.

Voids

Large voids are readily identified and estimating their volume in composites is a routine operation. But more sensitive detectors have to be found for tracing internal crazing. The problem becomes even more pressing if the fatigue properties of composites are taken into account. The makers of glass fibres advocate¹⁸ the following design safety factors for glass reinforced plastics (GRP) composites: static long term loading one fourth of the static strength, dynamic fatigue one fifth and impact loading only a tenth of the static strength. In other words high modulus fibre composites are *unsafe at almost any impact*

load. The experienced designer, therefore, inserts a piece of tough metal at critically loaded areas of filament structures¹⁹.

The growth of voids at the interface is a frequent cause of debonding. As pointed out above, the consequences of dilatational strains and stresses at the glue line are difficult to predict. In a stressed rubbery adhesive the negative hydrostatic pressure can lead to growth and cavitation of initially small voids, as was shown by Gent and Lindlay (ref. 1, p. 85–87). Recently Gent and Tompkins have extended this to the stress analysis of rubber systems containing gas bubbles²⁰ and fillers²¹. Their results are in good agreement with technological experience. Unfortunately, this successful model of incipient cavitation in rubbers is not applicable to hard polymers. However, Gent suggests²² that glassy plastics undergo stress-activated softening at the tip of fissures and subsequent cavitation is then assumed to take place under the action of dilatant stresses. An extensive literature exists on fibre “pull-out” mechanisms. It would seem that the cavitation model, proposed by Gent, could also be of some help in the diagnosis of fibre-matrix “friction”.

Failure criteria

Although a bewildering number of fracture modes, testing procedures and field observations obscures the view, a unifying approach is within reach. There are two types of failure:

Type 1 failure: due to a controlled rate of cracking, arising from a steady rate of stressing;

Type 2 failure: due to catastrophically fast crack growth.

Whether fracture phenomena are experienced as adhesive or cohesive fracture (see Session V of this symposium), does not influence this classification; a generalized Griffith-type energy criterion serves as a starting point for a discussion of *controlled cracking (type 1)*. Continuing from the earlier work on the rupture of polymers²³, Gent *et al*^{24,25,26} have shown that the critical failure energy of an adhesive is determined by the viscoelastic response of the adhesive. Results therefore can be plotted in a so-called WLF strain rate-temperature scheme. Two factors were frequently ignored in earlier studies: (i) viscous losses during fast straining of the adhesive are *not* identical with the anelastic processes measured in thermodynamic equilibrium; (ii) maximum failure energy is obtained only if the adhesive is fully strained to its limit. Taking these criteria into account, adhesive and cohesive failure in tensile, shear and peel tests can be correlated^{25,26}. A wide range of technological tests, from the peeling of adhesive tape to the climbing drum testing of metal laminates, is now accessible to analysis in terms of continuum

mechanics. The trend of type 1 failure becomes then *predictable* from the known viscoelastic properties of the adhesive.

The designer, however, demands safeguards against the *catastrophical, type 2, failure mode*¹¹. Even a rubber disk will fracture “brittle” at low nominal strains, when it is severely constrained as in the Gent-Lindlay experiment mentioned above. These catastrophical failures are not predictable, unless the local stress distribution on loading is known in detail. Adhesion failure of a *low modulus*, rubber-like interface is also experienced when reflecting stress waves meet at this interface. A case in point is the erosion of coatings by raindrop impact at or above Mach-one speeds²⁷. A thin layer of *high modulus* binder or the resin matrix in a highly filled composite will always experience local multi-axial stress conditions and fail therefore in fatigue or on impact as GRP-composites do¹⁸. In all such cases of localized failure, monitoring of the rate of destruction by non-destructive methods is needed, but techniques are not yet available.

Physical and chemical creep

Stress relaxation by creep is sometimes acceptable to the designer, at least if the creep rate can be predicted. The basic *physical* processes are fairly well understood, but *chemo-relaxation* also occurs: Observations on the behaviour of polysulphides led Tobolsky, many years ago, to propose a stress-induced rapid interchange of primary bonds. To-day chemo-relaxation is a possible design factor in laminates, intended for high-temperature service. No means are yet available to control and predict *chemo-relaxation at chemically modified interfaces*. Stress-optical analysis of interfaces, a possible approach, is beset with experimental difficulties. Optical sectioning by micro-holography of the glue line might become useful in future interface analysis.

Life expectancy

The ultimate aim of mechanical testing is a reliable prediction of failure limits and of fatigue life. In laminated metal structures the plastic reserve of metals and of tough adhesives can be combined to a composite that will “fail safe”, if at all. Still, more detailed information on the nature of stress relaxation would be welcome even here. Unidirectional, stiff fibre composites have very little plastic reserve and early detection of fissures is needed to avoid further disappointments⁵ in practice.

In the rush for lighter and stiffer composites, known methods of fissure analysis have not been used to the full extent. For example, Bernard Rosen used the strain-enhanced helium transport through brittle polymers, as a probe for the growth and healing of micro-fissures²⁸. This technique might

be a candidate for fatigue analysis of layer structures. Further, the chemist would like to identify gases and vapours, released during ageing of bonded systems. Analysis of sub-microgram quantities in the vapour phase is now performed routinely in biological research. Perhaps the elegant torsional braid technique of Armand Lewis²⁹ could be adapted to this purpose.

INTERFACE SYSTEMS AND THE METALLURGIST

Optimum properties of jointed mechanical systems can be obtained only if matching interfaces are "optimized" to this purpose. Surface modification of metals, glasses, ceramics or polymers will improve "adhesionability", but at the same time the treatment might reduce stress corrosion resistance and/or dynamic fatigue life of the adherend. Depending on the economical or social importance of the problem, detailed analysis of surfaces and their interaction will be needed. Progress then depends on available tools and the scope of their application.

Surface analysis

Some methods of interface³⁰ and of surface³¹ analysis have been discussed recently. Three general techniques deserve special mention. *Microprobe analysis* permits the identification and localization of elements in small surface areas (microns²). Recent instrumental improvements have led to an extension to lower atomic numbers, including (bio)organic matter; more important, the method can be applied to *amorphous* volume elements. Low energy electron diffraction = *LEED* analysis yields detailed information on crystal structures in the outermost surface layer, as such it is of significance in structure analysis of catalysts or semiconductors, rather than adherends. However, *Auger spectrometry*, mostly used in conjunction with LEED, has given unique insight into the onset of metallic adhesion, at high optical resolution (Angstroms).

Interacting metallic surfaces

The well-known work of Krupp and his associates (ref. 2, p. 6) on the *reversible* adhesion between little gold spheres and solid surfaces has led to quantitative expressions, not only of the magnitude of intermolecular forces, but also of technological parameters, e.g. surface roughness, moisture, influence of surfactants, etc. As considerable skill and time is needed, application of the analysis will remain limited, moreover it is not well-suited to adaption for uhv conditions.

When clean and pure single crystals of metals are placed upon each other in an uhv, cold welding takes place immediately. Buckley^{32,33} has studied

this *transition from adhesion to cohesion* at the interface with the aid of LEED and Auger spectrometry. Atoms of the mechanically weaker metal are accommodated onto the surface of the stronger metal and an interphase is formed, although not all the details are yet clear³⁴; cohesive fracture occurs in the mechanically weaker link. The ease of this "diffusion bonding" depends, in part, on the mutual solubility of the pairs. The validity of "solubility rules" for metallic adhesion is restricted in the same sense as Voyutskii's adhesion rules for polymers; metallic adhesion can be produced by large plastic deformation alone, moreover traces of oxygen or sulphur have a profound influence on diffusion across the interface. But, the insight gained permitted the coining of a guiding "principle of compatibility" in tribo-engineering³⁵.

Keller has studied the influence of environmental impurities on the autohesion of silver, and also the effect of 65 ppm carbon in the surface on the autohesion of iron, using mechanical measurements as well as changes in contact resistance^{36,37}. It is evident from this and related work that the adhesion properties of metals are largely determined by surface impurities. In general, however, we have to deal with metal oxides rather than with metallic surfaces. This concept of adhesion and cohesion expressed in terms of "solid state chemistry" will influence future events in the technologies of sintering and friction welding.

Clean and oxidized metallic surfaces

The interaction of inorganic liquids and liquid metals with high energy surfaces is difficult to calculate. Practical examples are the high contact angle of liquid glass on noble metals and the spreading of liquid gallium on clean nickel. Certain considerations regarding the structure sensitive properties of water led Bowden and later Fowkes to the conclusion that water should not spread on clean noble metals (ref. 1 p. 24 and 44, 45). Indeed careful experiments by Erb and by White apparently proved the hydrophobic nature of oxygen-free high-energy surfaces (ref. 2 p. 45 and Table I). However, Bennett and Zisman have recently shown that pure water is spreading spontaneously on a smooth, clean, pure gold surface.³⁸ These results suggest that the data published by White were influenced by the presence of hydrophobic trace impurities on the gold surface. Using an ultra-high vacuum technique Schraders³⁹ proved that condensing water droplets will spread on gold surfaces, contrary to the earlier results reported by Erb. The controversy, which presumably will be discussed during the first session of this meeting, illustrates the extreme difficulties encountered in producing a "clean" surface. Schraders results are in line with the well-known large influence of trace impurities on the friction between pairs of metals in an uhv.

Most metals are covered with an oxide layer, they should be hydrophilic. White⁴⁰ has shown that carefully oxidized metal surfaces, exposed to laboratory air, are rapidly covered with organic materials and then they react hydrophobic. This adsorption of organics is *reversible*, the impurities can be desorbed in a desiccator over activated aluminium. Oxidized metals differ widely in their sensitivity to atmospheric impurities: An oxidized nichrome surface adsorbs organics faster and desorbs them slower than an aluminium surface⁴⁰. The metallurgist is given here a simple, but sensitive tool to analyze adsorption and wetting properties of metals.

Adhesionable surfaces

Certain concepts in technology cannot be reduced to measurable quantities. In this respect “adhesionable” surfaces are on a level with “oiliness” or “lubricity” of lubricants. In cleaning a surface or changing the roughness many parameters can be altered simultaneously: composition, accessibility, reactivity, brittleness, hardness or modulus, but also the ability to influence condensation or crystallization of the counterface. A unifying method, permitting transfer of experience from an assembly of case analyses is needed. “Dynamic Systems Thinking”⁴¹ might be effective in the long run.

PRODUCTION ENGINEERING PROBLEMS

Countless generations of carpenters prepared the ground for the rapid, large scale production of glued wooden aircraft and gliders, when they were most needed in Great Britain (ref. 11, p. 152–161). This “wooden” tradition of cleanliness and precision (ref. 11, p. 161) was carried over to the new technique of laminating metals (Schliekelmann, ref. 2, Chapter 15), which has already found many engineering applications⁴². But the “adhesionable” properties of etched metals have still to be established by trial and error⁴². Optimum surface quality of aluminium seems to be linked to a certain degree of micro-roughness (50–100 Å)¹⁹, at least with certain structural adhesives. Chemical stabilisation of the oxide layer will depend also on components of the etching fluids, however, details of aluminium surface chemistry are extremely complex⁴³. Mechanically identical metal sheets, obtained from different suppliers, do not have the same “adhesionable” quality after etching. Corresponding problems exist for glass and graphite fibres. The engineer is thus forced to apply rigorous quality control and to search for less “surface-structure sensitive” curing methods, suitable for mass production.

Acoustical quality of glued containers was first assessed by Antonio Stradivarius. Presumably, the sensitivity of his manual test is difficult to

surpass, but equipment has since grown vastly more complex. Entirely new chances of inspection are offered by holography and by infrared-thermography, applied not only in structural testing, but also in tracing the decay of decorative and protective coatings.

A frequent cause of adhesive or cohesive failure is the unintentional built-up of internal stresses, due to shrinkage on curing, to changes in humidity or to differences in the coefficients of thermal expansion (ref. 1, p. 63; ref. 2, p. 21). The great practical importance of these factors has not yet been matched by systematic adhesion studies. Quite to the contrary, the effect of thermal expansion is sometimes overlooked, but not for long^{5,19}.

Complex curing cycles or long "drying" times are an impediment to mass production. Engineers pioneered solutions of their own. Electron beam curing has given a new dimension to protective coating production. Sputtering, originally a 19th century curiosity, is now a means of transferring fragments of solids onto almost any surface, thus producing a dense and strongly adhering layer. The time-lag between these practical successes and their ad hoc theoretical interpretation constitutes a gap of considerable magnitude.

ADHESION, THE SURGEON AND THE DENTIST

The application of adhesives to calcified tissues, i.e. bone, dentine and enamel, is still in its infancy⁴⁴. Bone is a spongy composite of complex structure^{11,44,45}. When loaded at low strain rates the fracture energy of bone is high, comparable to that of a tough metal, while on impact loading bone breaks like a brittle plastic⁴; An adhesive, meeting these mechanical requirements while conforming also to the cellular bone surface is difficult to visualize. Acrylic cements are used in hip surgery for the fixation of a metallic femoral head prosthesis into the bone cavity⁴⁶. The low apparent density of the hardened cement, as well as SEM pictures⁴⁴ show clearly that the cement has a spongy structure and therefore adapts well to the bone surface. Surgeons^{44,46,47} agree that the set cement does *not* function as an adhesive, but only by mechanical interlocking. This 'bonding' process is comparable to the repair of machine parts by gap filling anaerobic hardening 'adhesives'. Such cements can sustain high loads in compression, but not in tension.

Dentine consists of highly orientated apatite-type crystals bonded by an organic (mostly collagen) matrix. D. C. Smith⁴⁴ has developed polycarboxylate cements that display true adhesion to the surface of dentine and even to enamel under oral conditions. Choice of the correct surface preparative methods to produce clean adherend surfaces is important for permanent bonding. However, the coefficient of thermal expansion of polymers is much larger than that of dentine. This factor alone is, no doubt, responsible for some of the many disappointments, experienced with cavity filling polymers

in dentistry. The social and economical importance of dental restorative materials is an incentive to further research, which should be stimulated by the advances reported at this symposium.

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