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### Some Analytical and Theoretical Aspects in Adhesion Science

W. Brockmann<sup>a</sup>

<sup>a</sup> University of Kaiserslautern, Kaiserslautern, GERMANY

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# Some Analytical and Theoretical Aspects in Adhesion Science

W. BROCKMANN

*University of Kaiserslautern, 6750 Kaiserslautern, GERMANY*

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Two examples will serve to demonstrate that progress in adhesion science depends on more than sophisticated analytical techniques. Examining simple models of adhesional interactions, or of the state of surfaces, can lead just as well to a better knowledge of what is often called the phenomenon of adhesion.

## 1 INTRODUCTION

If the origin of adhesion science is dated from the basic publications of Young<sup>1</sup> or Volta,<sup>2</sup> this field of natural science is now nearly 200 years old. The first half of this period was characterized by mostly theoretical considerations while the second half and particularly the last thirty years, has been influenced by the dramatic development of experimental and analytical techniques. The progress is impressive. For example, the nearly complete solution of the problem of adhesion durability in bonded aluminum parts of aircraft in the late eighties is unthinkable without the help of modern analytical techniques like Transmission Electron Microscopy and Fourier-Transform Infrared Spectroscopy.<sup>3</sup>

Nevertheless, the state of knowledge today is not completely satisfactory because many very simple questions remain unanswered. Two examples will serve to demonstrate this situation.

## 2 WEAK BOUNDARY LAYERS

Since Bikerman<sup>4</sup> published his book in 1961, the adhesion community has been discussing the question of whether weak boundary layers, for example in a polymer near a metal surface, could exist and, if so, how they could be created. Some scientists have rejected their existence or importance, while others have tried to explain them by mechanisms like selective adsorption due to the influence of a solid surface on which the polymer is formed.<sup>5</sup>

Today we know that weak boundary layers, for example in bonded metal joints, can exist<sup>3</sup> and can be detected by wedge tests or wet peel tests. But the reason for

their existence and their true nature could not be fully explored by analytical methods until today.

In this context, it seems surprising that a very simple model experiment proposed by Kollek<sup>6</sup> leads to a better insight into this mechanism. He took simple wooden balls of different colors from the toy box of his small daughter and bonded to their surface small pieces of so-called Scotch mate tapes with which mechanical joints between textiles are normally produced. As depicted in Figure 1 in this way a very simple model for polymerization reactions is created; in this case, a model of polyaddition in which grey balls can be joined only with black balls, but not with other grey balls. Several of these balls, with the tapes as "reactive sites," are placed on a household board as shown in the top part of Figure 2. One of the sides of the board is also equipped with other tape pieces as possible "adsorption sites" for some of the "molecules." Shaking the board now leads to a depiction of polymerization in the presence of a surface, as shown in Fig. 2, bottom.

When this simple experiment is repeated again and again it is apparent that the polymer structure particularly voids and orientation in the boundary layer looks different than in the bulk polymer. This difference is due to the fact that the mobility of the initial "adsorbed" individual molecules at the solid surface is limited by the adsorption process, which in turn influences the cross-linking density and which can create orientation effects during the polymerization process.

This simple experiment is convincing proof that a weak or at least influenced boundary layer must exist in a polymer if it is polymerized in the presence of an active surface which is needed to produce good and durable adhesion.

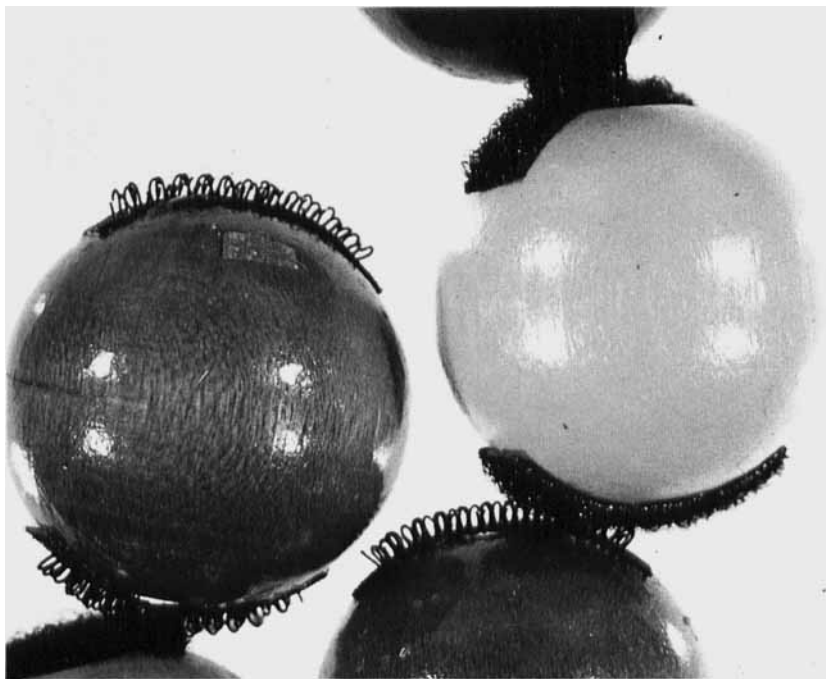


FIGURE 1 Simple polymerization model. See Color Plate I.

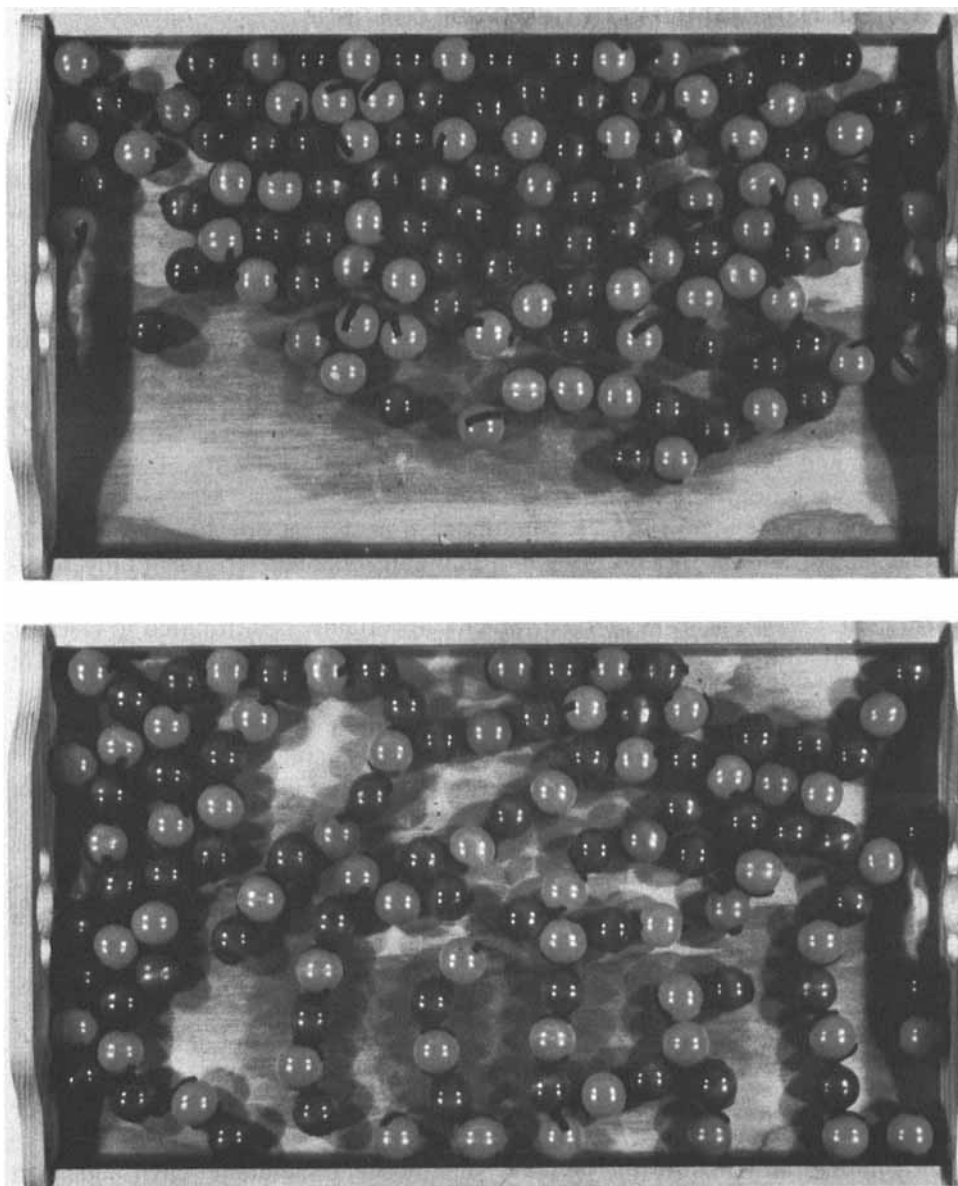


FIGURE 2 Monomers before "polymerization" (above) and after "polymerization" in presence of reactive surfaces (bottom).<sup>5</sup> See Color Plate II.

By further refinements of such experimental models, for example, using Stewart models in the presence of real surface configurations on the same scale, more information about the state of a real polymer created in the presence of solid surfaces can be obtained. It is doubtful whether information about the polymeric structure in such small dimensions is obtainable using analytical techniques.

### 3 ADHESION OF METALS WITH THIN OXIDE COATINGS

Aluminum and titanium alloys have been favorite subjects of adhesion research work due to the fact that they are the most important materials in the aircraft industry. Their popularity as subjects for study is fortunate for today's researchers because these alloys have relatively thick oxides on their surfaces from the common chemical treatment methods used in the aircraft industry. Their resulting configurations are particularly well suited for study using ultra-thin cross-cuts in the Transmission Electron Microscope. The situation is totally different if steel is the substrate examined. For example, mild steel in the automotive industry is adhesively bonded as received from the rolling mill using specially formulated adhesives which can remove or dissolve the corrosion inhibiting oils. Scanning Electron Micrographs of such surfaces taken under magnifications of 2,000X or 20,000X show more or less cleft topographies without the porous oxide structures which are typical for aluminum and titanium. In contrast, using the TEM the steel surfaces appear relatively tight and heavy.

Examining these steel surfaces using modern analytical procedures like EDX, AES, XPS, or SNMS, the following information is obtained. Iron naturally dominates the surface whereas oxygen, present in relatively small amounts, is not equally distributed. Carbon is also observed, which can certainly be attributed to residues of rolling oil. Sometimes some sulphur is present, and, depending on the quality of steel, also small amounts of aluminum.

The reaction product between iron and oxygen on a mild steel surface is mainly polycrystalline  $\text{Fe}_2\text{O}_3$ . The thickness of oxygen containing layers is normally not greater than 1 nm. Iron-oxygen combinations or compounds are present in about 2.5 nm atom layers. In the Transmission Electron Microscope (300 kV at 2,600X magnification), ultra-thin cross-cuts from the boundary layer section of steel show the morphologies as seen in Figure 3.

The electron micrograph of the rolled steel surface shows a surface profile with a roughness depth of around 0.1  $\mu\text{m}$  with undercuts. Such a geometry cannot be detected with normal roughness measurement techniques which generally would give a roughness value of around 1.3  $\mu\text{m}$  for rolled steel. In the recognizable undercuts there are still some residues of rolling oil which are not uniformly distributed. The smallest recognizable structures in this picture have dimensions of nanometers. The distinct formation of oxide structures, as observed on aluminum or titanium, seems not to be present.

Calculating the length of the boundary line between metal and environment in the same dimension as the perceptible roughness (micrometer dimension) leads to the result that the boundary line must be about three times longer than the picture diagonal which can be approximated as the geometric measured boundary line. The size of the surface in the depicted section is therefore already about 4 to 5 times greater than the one measured geometrically. Introducing this size of surface in the above mentioned estimation of oxide thickness from the micro-analysis, the surface is coated by only about 5 atom layers of oxygen containing products. Following this calculation to a first approximation, a closed or a tight oxide layer seems to be improbable.



FIGURE 3 Transmission Electron Micrograph of an ultra-thin cross-cut on the boundary of rolled steel.

On speculation, the situation becomes more complicated because a further study of Fig. 3 leads to the conclusion that the real boundary line of the cross-cut, and in turn the area of the surface, can be determined by smaller structures than the roughness or undercuts.

A simple example shows the basis of such speculation: Looking down through the window of an airplane on a clear day at an altitude of about 10 km, one can distinguish between things like windows in houses or small trees at a coastline in the dimensions between 2 and 10 m. With such lateral resolution, for example, the length of a coastline between a beach and the ocean could be registered technically. However, sitting directly on the beach after the flight it becomes clear that the real length of coastline between beach and water is not determined by structures in the dimensions of meters, but by the diameter of the sand grains at the beach, which is in the dimensions of 0.5 or 1 mm. This realization leads to the conclusion that the real length of the coastline must be 100 times larger than the length calculated using observations from an aircraft.

Coming back from the beach to the laboratory and observing a rolled steel surface with some scratches, visible to the naked eye, one can state that scratches between 1 and 10 micrometers in width are detectable. Comparing this experience with the fact that in the electron micrograph in Fig. 3, a particle dimension in the nanometer scale determines the real length of boundary between steel and environment, it becomes clear that the real length of the boundary line, just as at the beach, may

also be 100 or 1,000 times higher than what is geometrically measurable. If this is true, then the often postulated existence of a totally closed oxide layer becomes more and more improbable. Back to the beach this should mean that between the many interfaces of white sand grains dominating the beach, a few black ones must be present. To what extent these black grains dominate the properties of the beach remains an unanswered question.

Some objections against such a simple calculation or speculation are possible. According to our present understanding of the state of materials, a transition between iron and the environment without a chemically stable oxide layer is unimaginable. But the fact that on such thin oxide coated metals very good adhesion is obtained in many cases leads to the idea that this kind of adhesion is not dominated by the oxides, but more by the base material, which can react through the oxides directly with the prepolymeric molecules. This reaction happens in a similar manner as, it is assumed, occurs in the vulcanizing of rubber in the presence of surfaces of copper-containing alloys.<sup>7</sup>

Such a direct adhesional reaction, "through the oxides" between the base metal and the organic substances, for example by chelation bonds, provides an explanation for the good durability of adhesion. In this way the thermodynamically unstable oxides cannot dominate the behavior of the adhesion zone.

The hypothesis that direct adhesional reactions between the surfaces of base metals and organic substances may be possible is supported by the fact that on plastically deformed metal surfaces (for example after grit blasting processes) good and water-stable adhesion between metal and polymers is frequently observed. Plastic deformation increases the chemical reactivity of the metal, as can be seen in corrosion tests, or by the increased exo-electron emission. In many cases, very thin oxide layers are measurable on plastically deformed metal surfaces, particularly on steel. These observations allow one to conclude that a direct reaction between the activated base metal and the prepolymeric resin is possible.

It seems that in adhesion science two ways will lead to progress. One is the further development of the present analytical techniques in the direction of higher lateral resolution making it possible to study chemical structures in very small dimensions. On the other hand, it may be that relatively simple and cheap model experiments can be designed to ask, for example, of the steel surface, "What are you?" and by using an experimental result obtained by Plinius junior, published in the literature of ancient Rome. He found out that Gallus acid reacts slowly with iron—as we know today in the form of an absolute water-stable chelate complex which is black. He introduced this reaction into black reaction products for the analysis of iron in different substances. The same procedure is possible on steel surfaces if they are stored in organic solvents containing Gallus acid for 10 to 30 min. under normal temperatures. After some hours the steel surfaces become grey or black, and this color is not easily removed by water. The behavior of the steel surfaces in this experiment is, following the reasoning of Plinius junior, simply that of iron. Oxides on the surface are present, but iron is the dominating substance. Is adhesion, then, only a problem of the surface, or can it come "from the deep"?

These ideas about adhesional mechanisms may be concluded with a statement by Sir Issac Newton shortly before his death: "I do not know what I may appear to the

world, but to myself I seem to have been only like a boy playing on the seashore, and diverting myself in now and then finding a smoother pebble or a prettier shell than ordinary, whilst the great ocean of truth lay all undiscovered before me.”

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