Metal-Polymer Systems
Interface Design and Chemical Bonding
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Interface Design and Chemical Bonding

Jörg Friedrich
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Preface

Recently, a great variety of books on adhesion, written by well-known and excellent researchers, is available for the readers in science and industry. Composite materials and adhesives, metals, and welding become important to discuss adhesion.

Focus of research on adhesion gives the scientific explanation of the adhesion phenomenon from physical or technical perspective. The industrial interests are more focused on adhesive, primer, or glues, their production, composition, and processing.

This work discusses the chemical processes that play a role in the adhesion phenomenon, however, now from the polymer point of view. It also considers chemical and structural changes in the involved materials of composites contacting at the interface. To join different materials well, adherent, the interface, and their structure become significant.

The book focuses and intends also the intensified consideration of chemical processes along and across interfaces. It emphasizes the role of permanent, durable, and strong chemical bonds at the interface. Ultimately, it recommends the systematic synthesis of covalent bonds across the interfaces, which are favored compared to weak and sensitive physical interactions.

By means of several examples, the general molecular structure of an efficient construction of interface is introduced. The aims of new different interface elements are explained. The final goal of interface structuring is the mechanically and hydrolytically non-separable composite. By means of aluminum–polyolefin composites with extraordinary adhesion and durability, such behavior is technically realized.

The author was engaged in this field from the beginning of his scientific career as PhD student in 1972. In particular, he thanks his former supervisor Dr. habil. Joachim Gähde, who was and is a great guide in science. Several former colleagues are involved in the author’s work and have contributed to many published scientific papers, including Mrs Dr Ingrid Loeschcke, who had measured materials with X-ray photoelectron spectroscopy since 1973. To bear in mind that the author, who was incorrect in political affairs and did not follow the official directives in former German Democratic Republic, nevertheless has got much support from the institute’s director Prof. Horst Frommelt and the chief of the Central Institute of Organic Chemistry in the former Academy of Science in Berlin, Prof. Hans Schick. Among the technical staff, Mrs Gundula Hidde has to
be emphasized. She has measured and prepared nearly all samples with excellent correctness, contributing own ideas, and produced results with high standard. Without her assistance, this book could not have been written.

I also have to thank my coworkers and colleagues. Dr Gerhard Kühn and Prof. Andreas Schönhals were my deputy chiefs in the Federal Institute of Materials Research and Testing in Berlin, since 1995, working on a high scientific level and were coauthors in many papers. The author of the book can only present some examples of excellent contributing coauthors, including Dr Harald Wittrich, Dr Wolfgang Unger, Prof. Heinz Sturm, Prof. Christian Jäger, Dr Asmus Meyer-Plath, Dr Sascha Wettmarhaus, Dr Rolf-Dieter Schulze, Dr Steffen Weidner, Dr Günter Schulz, Dr Jana Falkenhagen, Dr Ralph-Peter Krüger, Dr Simone Krüger, my daughter, Prof. Alaa Fahmy Mohamed, Dr Konstantyn Grytzenko, and so on.

There were also important input and support from anonymous scientists, such as from DuPont, Dow Chemical, BASF, Bayer, Ahlbrandt, Fluor Technik System and others. I give special thanks to Dr Pierre Lutgen for introducing me to the new world of science around DuPont in 1989. Much support was given by Dr Wolfgang Saur from Switzerland. Close fruitful and helpful contacts should also be mentioned to Prof. Christian Oehr, Dr Kashmari Mittal, Prof. Jose Miguel Martin Martínez, Prof. Voytek Gutowski, Prof. Michel Wertheimer, Prof. Wulff Possart, Prof. Farzaneh Arefi-Khonsari, Prof. Gerhard Blasek, Prof. Claus-Peter Klages, Prof. Hideyuki Sotobayashi, Prof. Eldar Bahadur Zeynalov, Prof. Norihiro Inagaki, Prof. Jürgen Meichsner, Prof. Hans-Ulrich Poll, Dr sc. nat. Helmut Drost, Prof. Hans-Jürgen Tiller, president Prof. Manfred Hennecke, Prof. Andreas Hampe and others.

Without the contributions of coworkers, colleagues, and partners this book would not exist.

I thank also the publisher Wiley-VCH and its coworkers for having given me the opportunity to illuminate the “old” adhesion from the “chemical” point of view.

Last but not the least, I have to thank my wife, Dr Waltraud Friedrich, my daughters, and all my grandchildren for understanding that I have blocked little time for my great family. And, not to forget, I have to thank my parents, in particular my father, who introduced me to natural science, who was a generally educated scientist of chemistry, food chemistry, pharmacy, and medicine.

Berlin, August 2017
High-Performance Metal–Polymer Composites: Chemical Bonding, Adhesion, and Interface Design

1.1 Introduction

Most published books on adhesion are focused on the discussion of reversible physical interactions along the interface of polymers and coatings. Such adhesion can be described fairly well in terms of thermodynamics. In contrast, mechanical anchoring due to rough surfaces and mechanical interhooking is determined by mechanics. Chemical interactions or chemisorptions may be caused by hydrogen bonds produced by polar groups containing a covalently bonded H atom and an atom with a free pair of electrons. Oxygen and nitrogen groups are often involved in hydrogen bonds. Chemical bonds are often in focus of speculation but seldom clearly detected. Only in a few cases, chemical bonds between polymers and coatings were consciously prepared. This book will present some examples for systematic introduction of covalent bonds between polymers and coatings along the interface. The efficiency to form chemical bonds instead of physical interactions is high because of higher binding energies; thus, a strong adhesion promotion by dense chemical bonds is expected.

Sticking two solids together using vegetable resins is one of the oldest examples for adhesion in the history of mankind, at least in the period as Homo sapiens were arriving in Europe (about 40 000 years ago) [1]. It is also found that the foregoing species, the Homo neanderthalensis (180 000–30 000 years ago), may also be Homo erectus (1 000 000–180 000 years), invented glue as essential to produce their most formidable hunting weapon using bitumen or asphalt and heated it for better gluing. The finding in 1963 in Königsaeue is at least 40 000 years old, that in Campitello is 200 000 years old, and that in Inden-Altdorf about 128 000–115 000 years old (Figure 1.1) [2–4].

The base of this development of weapons was the found in the lances in Schöningen (Germany), more than 300 000 years old, hardened at the top by fire [5].

Now, let us consider the basics of adhesion in a composite or laminate. Two different solids with almost different chemical compositions, structures, reactivities, surface properties, and mechanical strengths collide in one atomic layer, and the transition from one to another solid takes place in one atomic layer. This transition from solid A to solid B is called interface (Figure 1.2).
This atomic gap between solid A and solid B has to be bridged by physical, chemical, or mechanical forces to achieve proper adhesion. Often, a clear transition from solid A to solid B in one atomic layer is not found. Adjacent to the interface, polymers often show a new molecular orientation caused by the interaction with the coating material. Such an example is the “trans-crystalline” orientation of polymers in coatings caused by the texturing action of the metal substrate [6]. This behavior is similar to that of the well-known epitaxy. Thus, the interface region of a composite or laminate consists of the ultimate interface, transition zones in the two neighboring solids (interphases), and the intact original morphology of the two solids (bulk) (Figure 1.3).

Often, contaminations and additives accumulated at the polymer surface, metal oxide skin, and aged and/or oxidized polymer species at the surface/interface hinder the direct interaction of the two solids in a laminate.

Another problem is the contact area between two solids. The greater the contact area, the higher is the concentration of interactions and the stronger is the adhesion. Thus, roughness can increase the contact area, when one solid can wet and, therefore, adapt the rough surface topography of the other solid (Figure 1.4). Such adaptation occurs when the coating is evaporated, molded, or is a dip- or spin-coating film.
1.1 Introduction

Figure 1.3 Examples of the schematic design of metal–polymer interfaces with interphases and the original bulk materials.

Figure 1.4 Problems with minimum contact area in case of laminating rough surfaces.
Now, let us have a look at the binding energies of interactions between two solid phases. The energy of interactions grows moderately from physical interactions to hydrogen bonds. Nevertheless, such van der Waals interactions and hydrogen bonds have low binding energies in comparison to those of chemical bonds. However, such low binding energies can be compensated partially by a high concentration of such interactions, that is, the addition of such many very weak interactions results in a great sum, also in strong adhesion in comparison to rare strong chemical bonds (Figure 1.5). The conclusion is that a great number of strong chemical bonds are needed to achieve a maximum in adhesion.

It will be shown in the following chapters that a high density in chemical bonds across the interface can be realized. However, in such a case, two new difficulties appear. First, the chemical bonding across the interface is equal to or even stronger than the bonds in the polymer represented by the cohesive strength of the polymer in laminate materials; thus, the failure at mechanical loading shifts from the interface to the polymer bulk, termed as cohesive failure (Figure 1.5).

And, secondly, the chemical bonding makes the interface inflexible, and at mechanical loading, adjacent material layers fail (near-interface failing). To avoid such failing by stiffened near-interface layers, flexibilization of the interface is needed as realized by long-chain aliphatic spacers or viscoelastic polymer adhesion-promoting layers (Figure 1.6).

Chemical bonds across the interface between two polymers are most often covalent bonds, such as C—C, C—O—C, CO—O, CNH$_2$—O, etc. bonds. Their

![Figure 1.5](image-url)  
_Schematic comparison of the strength of interactions (bond dissociation energy) and the measured total adhesion between a polymer and a coating, depending on the type of interaction and the density of these interactions along the polymer–coating interface._
formation is possible by chemical reactions of different functional groups of the two laminated polymers, by graft reactions or by use of peroxide for linking. The bond strengths of such covalent bonds are in the range of 350–400 kJ mol\(^{-1}\) or more, greater than the physical interactions by a factor of at least 100.

If the polymers are compatible in a thermodynamic sense, that is, have similar structure or equal chain segments, interdiffusion may also occur [7]. The compatible chain segments of polymer A and polymer B interpenetrate in a small interface layer. Solvent-induced swelling or heating supports interdiffusion. In such a case, the relating polymers A1 and A2 can coil in the interdiffusion zone as the macromolecules of a homopolymer. This molecular entanglement provides adhesion strength along the (former) interface similar to the cohesive strengths of polymers A1 and A2.

Functional groups on polymer surfaces or introduced on polyolefin surfaces can react with metal atoms or with its hydroxy groups at the surface of the oxide coating of the metal to chemical bonds (Figure 1.7).
The aim of this book is to overcome simple physical interactions in composites and to establish, in the adhesion community, new polymer pretreatment processes, new interface design by more chemical processing.

The higher binding energy, at least one order of magnitude, achieved by chemical (covalent) bonds compared to physical interactions between polymer and coating molecules should increase the adhesion in laminates and composites considerably. Thus, if covalent bonds are more densely distributed across the interface, a significantly higher adhesion in laminates or composites should be achieved. It can be compared with the cross-linking of polyolefins by peroxides producing a harder but more brittle polymer bulk with all its advantages and disadvantages.

Now, two solids are strongly bonded together by covalent bonding; however, the interface is simultaneously made more stiff and inflexible. Thus, the mechanical loading is redistributed from the interface in the (often) weaker solid, and the failure is relocated to the vicinity of interface as determined by interfacial thermodynamics and formation of internal stress [8]. Strong interfacial covalent bonds weaken the adjacent covalent bonds in the solid. For example, in polymers, the failure propagation changes from the interface to such weaker near-interface layer, which is associated with a considerably lower adhesion. It was shown that peeling is always assisted by internal stress, here, caused by strong covalent bonds along the interface and by different thermal expansion, whether tensile or compressive, because the stored elastic energy released by mechanical separation of the joint can drive the crack through the weakened near-interface layer of the polymer [9]. Such simple dislocation of failure to near-interface weakened polymer layers is not the optimum solution of the adhesion problem, but it is a significant advantage compared to a poor interfacial failure.

Many additional dispositions have to make for adhesion improvement in polymer composites than the introduction of chemical bonds. For example, flexibilization by spacer molecules or viscoelastic polymer layers, barrier formation against water, and ion diffusion and water repellence from interface to avoid hydrolysis of polar covalent bonds belong to such additional requirements. Such special design of the interface will be discussed later in detail.

Goal of adhesion promotion by introduction of chemical bonds is to generate a polymer–coating composite, which cannot more be separated mechanically and which is long-term durable also under heat and humid conditions [10].

Polyolefins have no functional groups, which can serve as comfortable anchoring points for chemical bonding to a coating. Thus, the surface of polyolefins has to be equipped artificially with reactive functional groups of one sort as possibly to form covalent bonds between polyolefin and coating. There are different ways to introduce such monosort functional groups on the surface of polyolefins, may be by blending or coating with adhesion-promoting polymers, copolymerization with adhesion-promoting comonomers, for example, maleic anhydride or physical, plasma-chemical or chemical surface modification [11].

With the introduction of such reactive groups to the polyolefin surface, a chemical reaction with reactive groups or atoms of the coating molecules can be started. This chemical reaction to form covalent bonds between the polymer substrate and the coating has often to be performed without the presence of
solvent. Therefore, prominent chemical reactions, such as nucleophilic substitutions, are not readily possible. Here, further investigation are needed, such as that made by Ertl for elucidation of catalysis mechanism [12].

In this context, it is important to note that the interface is often the boundary between two physically and chemically completely different solids, such as in case of metal-coated polyolefin foils. Two solid phases are confronted in one atomic layer, and the transition from one to another solid has to be achieved in one atomic layer. A long jump and, therefore, a strong gradient exist in different chemistry and physical behavior.

This abrupt transition from one to another type of molecules is now bridged by a covalent bond. It is easily understandable that such a bond is not a pure covalent bond. In case of a bond between polymer and metal phase, the polarity of such covalent bond is obvious. Moreover, the redox potential of metal is also of importance for the bond formation or for chemical reactions between metal and polymer, that is, it is significant if the metal is a noble metal or ignoble metal.

Thus, the binding energy of such a covalent bond between metal and polymer is in the same range of covalent bonds in polymer molecules (or even higher), but the long-term durability is very weak under ambient air conditions. The polar character of such bonds makes the bond easily attackable by humidity, by water, producing hydrolysis of bonds, for example, in Al-coated polymer laminates with Al—C or Al—O—C covalent but strong polar bonds: Al—C + H₂O → Al—OH + CH₄ and Al—O—C + H₂O → Al—OH + HO—C.

Penetrating moisture is a general problem in adhesion. Water films in the interface suspend the physical interactions because of the higher energy gain by the interaction of polar groups at the polymer surface with water molecules than with groups at the surface of the coatings with lower polarity (and lower surface energy). Hydrogen bonds were weakened, ionic as well as covalent bonds were hydrolyzed.

It should be added that two solids can also be strongly bonded together mechanically, by mechanical anchoring and interhooking with knobbled nodules and specially formed holes as known from anchoring of copper layers onto printed circuit boards [13] or by simple roughening and, therefore, increasing the contact area [14]. Such mechanical interlocking is also possible on a molecular level. Thus, the thermal welding of polymers [15], the autohesion of two pieces of the same polymer [16], the interdiffusion of structurally related polymers [17, 18], interface-crossing interpenetrating networks [19] are also possible. All this mechanical anchoring displaces the weak physical interactions by mechanical interhooking and utilizes the strength of polymer molecules, that is, the covalent C—C and C—O bonds of the polymer backbone determine the adhesion. However, the density of interhooking points is limited; thus, only a few backbones are used for adhesion. Therefore, such knobs and holes pull out under mechanical load.

This book focuses on the interface chemistry of chemical interactions, the mechanism of bond formation, the metastable situation of bonds producing hydrolysis and the thermodynamically driven redox reactions, the protection of polar bonds for hydrolysis and redox reactions by a barrier layer, the formation of a special interface design for substitution of physical forces by chemical
bonds, and the flexibilization by introduction of aliphatic spacer molecules. If the thermodynamically metastable situation of covalent bonds is addressed, then it will be shown later that such bonds tend to be transferred sooner or later to thermodynamically stable products, such as oxides or hydroxides or alcohols. The conclusion of this situation is that the polar covalent bonds have to be protected perfectly against hydrolysis and redox reactions to achieve long-term stability.

Chemical bonding to surfaces was termed as key factor for improved adhesion. Watts embosses the term “The Holy Grail of Adhesion” [20]. Chemical bonds as essential part of adhesion were assumed since the 1960/1970s, in particular with the introduction of silane coupling agents [21–23]; for example, glass fibers coated with aminosilane and embedded in epoxy resin show a continuous covalent bonding between fiber and resin (Figure 1.8).

The exact proof of the existence of chemical bonds was presented by means of X-ray photoelectron spectroscopy (XPS) [24]. The role of chemical bonds in adhesion was emphasized by Gähde [25] and Friedrich et al. [26].

Before substantiating the role of chemical bonds for adhesion promotion, the different types of interactions along polymer interface should be considered [27]: Keesom forces arising from molecules with permanent dipoles, Debye forces caused by a molecule with a permanent dipole inducing a dipole in a neighboring molecule by polarization, and London dispersion forces arising from instantaneous dipoles produced by the motion of electrons within the molecule [28–31]. The London forces (Heitler–London forces) are ubiquitous and account for a major part if not all of the strength of such polymers as polyethylene [30, 32]. All these forces are summarized as van der Waals forces [33]. Additionally, hydrogen bonds are also of significant importance below the energetic threshold to chemical bonds (Table 1.1).

Owens and Wendt propose that it is generally agreed in theory that attraction due only to secondary forces and hydrogen bonding is sufficient to produce
adhesive joints between polymers of strength equal to that of the polymers themselves without the need for chemical bonds. Since these forces decrease as the inverse sixth power of the distance between molecules, it is apparent that surfaces to be adhered must come into intimate, wetting contact [27]. Hydrogen bonds are a further force [34]. It is the electrostatic attraction between polar molecules that occurs when a hydrogen (H) atom is bound to a free electron pair of a highly electronegative atom such as nitrogen (N), oxygen (O), or fluorine (F). It is a strong dipole–dipole attraction [35]. Among the chemical interactions, the donor–acceptor interactions were made responsible for adhesion as well as [36] acid–base interactions [37, 38]. Colloid particles and their deformation at adhesion contact to a solid were considered [7], and contact-electrical phenomena also promote adhesion [39]. Forerunner of the electrostatic theory was the polarization theory, postulated by de Bruyne and Houwink [40].

In contrast to Owens and Wendt, other authors accept the existence of chemical bonds across the composite interfaces, even though van der Waals forces are dominating [41]. The significance of different forces and their contribution to adhesion were summarized in a few works [42].

Fowkes has proposed the simultaneous existence of the aforementioned different adhesive forces and has considered their contribution to the (measured) adhesion by its addition [36, 43, 44]. The work of adhesion (\(W_A\)) consists of dispersion (d), hydrogen (h), Keesom and Debye (k), acid–base (ab), and principally chemical bonds (cb): \(W_A = W_A^d + W_A^h + W_A^k + W_A^{ab} + W_A^{cb} + \cdots \) [41]. The surface free energy (\(\gamma\)) could be expressed in the same way in terms of contributions from the various interactions, \(\gamma = \gamma^d + \gamma^h + \gamma^x + \gamma^i + \gamma^{ab} \) [45], where the superscripts x represent dipole–dipole interactions; i, induced dipole–dipole. These relationships were often contracted to \(W_A = W_A^d + W_A^p\), where the superscript p represented all the polar nondispersion forces involved. \(W_A\) can be determined from contact angle data using the Dupré equation [46] for the reversible thermodynamic work of adhesion (\(W_A\)) to separate two closely contacting phases 1 and 2, \(W_A = \gamma_1 + \gamma_2 - \gamma_{12}\), where \(\gamma_{12}\) is the interfacial free energy between phases 1 and 2 [47–49].

The shortly introduced objectives and basics of adhesion should be discussed in more detail in the following chapters. The author is aware that there are many

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**Table 1.1** Interatomic forces in physical and chemical interactions.

<table>
<thead>
<tr>
<th>Forces</th>
<th>Energy (kJ mol(^{-1}))</th>
<th>Range (Å)</th>
<th>Radial decrease of energy</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Physical interactions (van der Waals)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dipole–dipole (Keesom)</td>
<td>20</td>
<td>3–5</td>
<td>(r^{-3})</td>
</tr>
<tr>
<td>Induced dipole (Debye)</td>
<td>2</td>
<td>3–5</td>
<td>(r^{-6})</td>
</tr>
<tr>
<td>Dispersion forces (London)</td>
<td>0.08–40</td>
<td>3–5</td>
<td>(r^{-6})</td>
</tr>
<tr>
<td>Hydrogen bonds</td>
<td>50</td>
<td>1–2</td>
<td>1.8 in water</td>
</tr>
<tr>
<td>Covalent bonds</td>
<td>400</td>
<td>1–2</td>
<td>Bond length</td>
</tr>
</tbody>
</table>
High-Performance Metal–Polymer Composites

books and encyclopedias written on adhesion of polymers. To add simply a new one is not fruitful. The author is also not a declared specialist on the development and interpretation of new adhesion theories. However, the author has introduced some ways for the introduction of chemical bonds across the interface; he has special knowledge on fitted interface design, has developed different tasks of interface design, has considered the chemical reactions passing the interface; and has also discussed other chemical problems in more detail. The reader should consider all chemical aspects of interface interactions and should be motivated to consider synthesis of an interface design, which is adjusted and specially tailored to polymer and coating structures. A few examples are presented to demonstrate such newly created interface designs. The thus produced outstanding results of adhesion measurement are discussed in the light of the special interface design. An ideal molecular arrangement along the polymer interface is discussed, and general limitations in adhesion improvement are also considered.

Nevertheless, some basics to polymer adhesion shall be presented to give the reader a more or less complete book on adhesion problems. However, techniques of adhesion measurement are omitted or only touched. Glues, adhesives, and silane adhesion promoters are not objects of this book.

Following this Introduction, general theories of adhesion and wetting, interactions at interface, polymer near-interface layers, the special situations at polyolefin surfaces, tasks of new interface structure, pretreatment of polyolefins, and achieved increase in adhesion by use of inserted spacer molecules are discussed.

References

2 Böeda, E. and Bonliauri, S. (2008) Middle Paleolithic bitumen use at Umm el Tiel around 70,000 BP. Antiquity, 82, 853–861.


40 de Bruyne, N.A. and Houwink, A. (1951) *Adhesion and Adhesive*, Elsevier, Houston, TX.
Interpretation of Adhesion Phenomena – Review of Theories

2.1 General

Adhesion is defined as sticking together of two materials [1]. Basic or fundamental adhesion means the summation of all interatomic and intermolecular interactions along the interface. There is the thermodynamically defined (reversible) work of adhesion (\(W_A\)), which is needed to disrupt the interface under equilibrium conditions. Such basic adhesion can be theoretically calculated, may be from contact angle data, which is based on Young’s equation [2] and Dupré’s equation [3].

Measured (practical) adhesion depends on the sum of all molecular interactions, mechanical interlocking, interface area (roughness), and properties of adjacent interphases. Interface is the boundary with molecular interactions between two materials, and interphase is the layer in a laminate material or in both adjacent to the interface. The interphase in material A is influenced in structure and composition by the adjacent material B and therefore by the interface A–B. In Figure 2.1, the locus of interface and interphases in a laminate are presented schematically by the example of a metal–polymer composite.

As it would be shown later in detail, two solids, brought together in a laminate, have thin surface layers with properties other than those of the bulk, such as contamination, oxidized material, different supermolecular structure, molecular weight other than the given. Additionally, the two solids influence each other and can undergo interface crossing (inter-)diffusions and chemical reactions, may be redox reactions. Moreover, practical adhesion is also determined by hydrolysis at the interface, diffusion of moisture to interface, which weakens the interface, crossing of diffusing ions and initiating reaction, and so on.

It should be emphasized again that among the “basic adhesion interactions,” chemical bonds produce the strongest input in adhesion. Therefore, the contribution of chemical bonds to the adhesion and the replacement of physical interaction by chemical bonds should be specially highlighted in this book.

It is usual to present a scheme of different types of adhesion and adhesion theories and related topics such as interphase, weak boundary layers (WBL), redox reactions. Such a scheme is more or less arbitrary and reflects the personal view on adhesion. Here, an additional attempt should be made (Figure 2.2).
Interpretation of Adhesion Phenomena—Review of Theories

Figure 2.1 Example of interface and interphase structure of a metal–polymer laminate.

Adhesion of polymers

Mechanical adhesion

Interphase formation

Mechanical interlocking

Increase of contact area

Inter-diffusion

Orientation phenomena

Internal stress

Chemically modified

Physical interactions

Electrostatic

Thermo-dynamics

Van der Waals

Hydrogen bonds

Coordulative bonds

Double layers

Inter-diffusion

Dispersive forces

Interaction Si-Na

Acid-base

Weak boundary layer

Surface energy

Dipole–dipole

Induced dipoles

Adhesion

Chemical interactions

Chemical bonds

Glues

Coupling agents

Figure 2.2 Overview on interactions along the interface and theories for their interpretation.

Another type of overview is depicted in Figure 2.3 with emphasis on molecular processes, shown schematically.

It should be mentioned that an interfacial or “adhesion” failure is very unlikely according to Bikerman; thus, often the interface is not the “weakest point” of a laminate [4].

Adhesion is macroscopically determined by a mechanical component or by electrical attraction or by welding. On this macroscopic scale, mechanical hooking and coiling by interdiffusion of related polymers are also possible or by the formation of interpenetrating networks (IPN’s). However, most often, adhesion
Adhesion mechanism

Figure 2.3 Overview on proposed adhesion mechanism.

means the interactions on an atomic or molecular scale [5, 6]. The formation of physical interactions is summarized in terms of van der Waals forces appearing after close contact and total wetting of the two phases of an adhesive joint. Chemisorption or formation of covalent bonds between polymers and coatings is the strongest linking of two phases. It can be compared with copolymers, where two different polymer units are connected by chemical bonds, thus neglecting their principal incompatibility. Chemical bonds across the interface of two solids are seldom because their formation needs reactive groups on both sides of the interface. Often, the formation of chemical bonds does not proceed spontaneously. Close contact, heat, solvent, and other preconditions have to be fulfilled.

Looking at the molecular interactions, taking the center of this book, their respective binding energies and their operating distance are of special interest. Van der Waals forces summarize dipole–dipole (Keesom), induced dipole–dipole (Debye), and dispersion forces (Heitler–London). In Table 2.1, the parameters of molecular forces are summarized.

Data of acid–base interaction were found in special books edited by Mittal [7], and ranges of interactions are found in Gutowski (cf. Figure 2.4) [8].

The approach of two molecules is very low (0.1–0.3 nm) before interactions or bond formation occur. Considering the often existing contamination layers on the surface of real solids, such needed near contact is prevented. Cleaning of surfaces by rinsing or extraction with solvents is required. Wetting the polymer surface by an adhesive applied in liquid phase or dissolved in a solvent adhesive
Table 2.1 Interaction forces and their ranges.

<table>
<thead>
<tr>
<th>Type of forces</th>
<th>Binding energy (kJ mol(^{-1}))</th>
<th>Operating distance (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical</td>
<td></td>
<td></td>
</tr>
<tr>
<td>van der Waals</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Keesom</td>
<td>20</td>
<td>0.3–0.5</td>
</tr>
<tr>
<td>Debye</td>
<td>2</td>
<td>0.3–0.5</td>
</tr>
<tr>
<td>Heitler–London</td>
<td>0.08–40</td>
<td>0.3–0.5</td>
</tr>
<tr>
<td>Hydrogen bonds</td>
<td>50</td>
<td>0.3–0.5</td>
</tr>
<tr>
<td>Chemical</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acid–base</td>
<td>20–190</td>
<td>0.3–0.5</td>
</tr>
<tr>
<td>Ionic</td>
<td>560–1000</td>
<td>0.1–0.2</td>
</tr>
<tr>
<td>Metallic</td>
<td>110–260</td>
<td>0.2–0.3</td>
</tr>
<tr>
<td>Covalent</td>
<td>60–680</td>
<td>0.1–0.2</td>
</tr>
</tbody>
</table>

Figure 2.4 Interatomic distances and bond energies in different types of physical and chemical bonds (A = reference atom, B = distances to the other atom depending on bond type).

also removes contamination layers and, moreover, brings mobility into chain segments located at the surface by swelling and solvatization effects. High mobility and solvatization effects are often preconditions for the formation of covalent bonds, for example, \(S_{N1}\) or \(S_{N2}\) substitution reactions. Viscous phases can also undercut contamination layers, and therefore, they are able to migrate to reactive groups of the polymer substrate and produce physical interactions. Formation of covalent bonds depends on viscosity and reactivity of glue or adhesive.