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Bodo Müller | Walter Rath

Formulating Adhesives and Sealants

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Bodo Müller | Walter Rath

Formulating Adhesives and Sealants

Chemistry, Physics and Applications

Bodo Müller/Walter Rath: Formulating Adhesives and Sealants

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Preface

Formulations of adhesives and sealants are listed in very few publications because they are closely guarded industrial secrets. Although guide formulations and patent examples are available, they cannot be used for a textbook without careful selection and revision beforehand.

This situation is similar to that for paint and coatings formulations. The recent textbook entitled "Coatings Formulations" shed light on the formulations used in coatings. It seems reasonable, then, that adhesives and sealants might benefit from similar treatment, with the aim of emphasizing the similarities between coatings and adhesives technology.

This book teaches adhesive and sealant formulation in two steps. Each section first describes the application and chemical basis of the type of adhesive or sealant concerned. This is followed by formulation advice and – if possible – an analysis of existing recipes (e.g. guide formulations and patent examples.) This analysis includes a calculation of the important characteristic values of the formulations. All calculations based on recipes and formulations are worked through step by step and should therefore be intelligible to beginners, too.

Of the many adhesive and sealant systems available, the selection provided in this textbook is restricted to the premium types. In a textbook, fewer, specific examples can prove to be more informative.

The formulations have mostly been developed from starting formulations or patent examples and cannot be used to produce adhesives and sealants without further ado. Moreover, starting formulations and patent examples are to some extent no longer state of the art.

Patent restrictions or registered trade marks (™ or ®) are not mentioned explicitly. Furthermore, it should be noted that product and trade names change as a result of mergers and acquisitions.

It has proved to be advantageous to classify adhesives (Part II) and sealants (Part III) by different criteria. In Part II, adhesive systems are classified by setting mechanism into physically setting, chemically reactive and pressure sensitive adhesives; applications are described as well. This type of classification is closely related to classification by the form of application. As sealants and adhesive-sealants, with the exception of the aqueous polyacrylates, are mostly applied in solventless form, it is beneficial to classify them by their applications in Part III.

This textbook seeks to familiarise laboratory assistants, graduates, engineers, skilled workers and chemists with the practice of adhesives and sealants formulation. It presupposes a basic knowledge of chemistry. It will also serve as a reference work for all readers interested in adhesives and sealants.

We would like to thank Ray Brown for polishing the text.

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January 2010

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Exclusion of liability

It should be noted that the contents of this book reflect the personal views of the authors, based on their own knowledge. This does not absolve readers of the responsibility of performing their own tests with respect to the uses and applications of the various processes or products described herein, and/or obtaining additional advice regarding same. Any liability of the authors is excluded, inasmuch as and to the extent permissible by law, subject to all legal interpretations.

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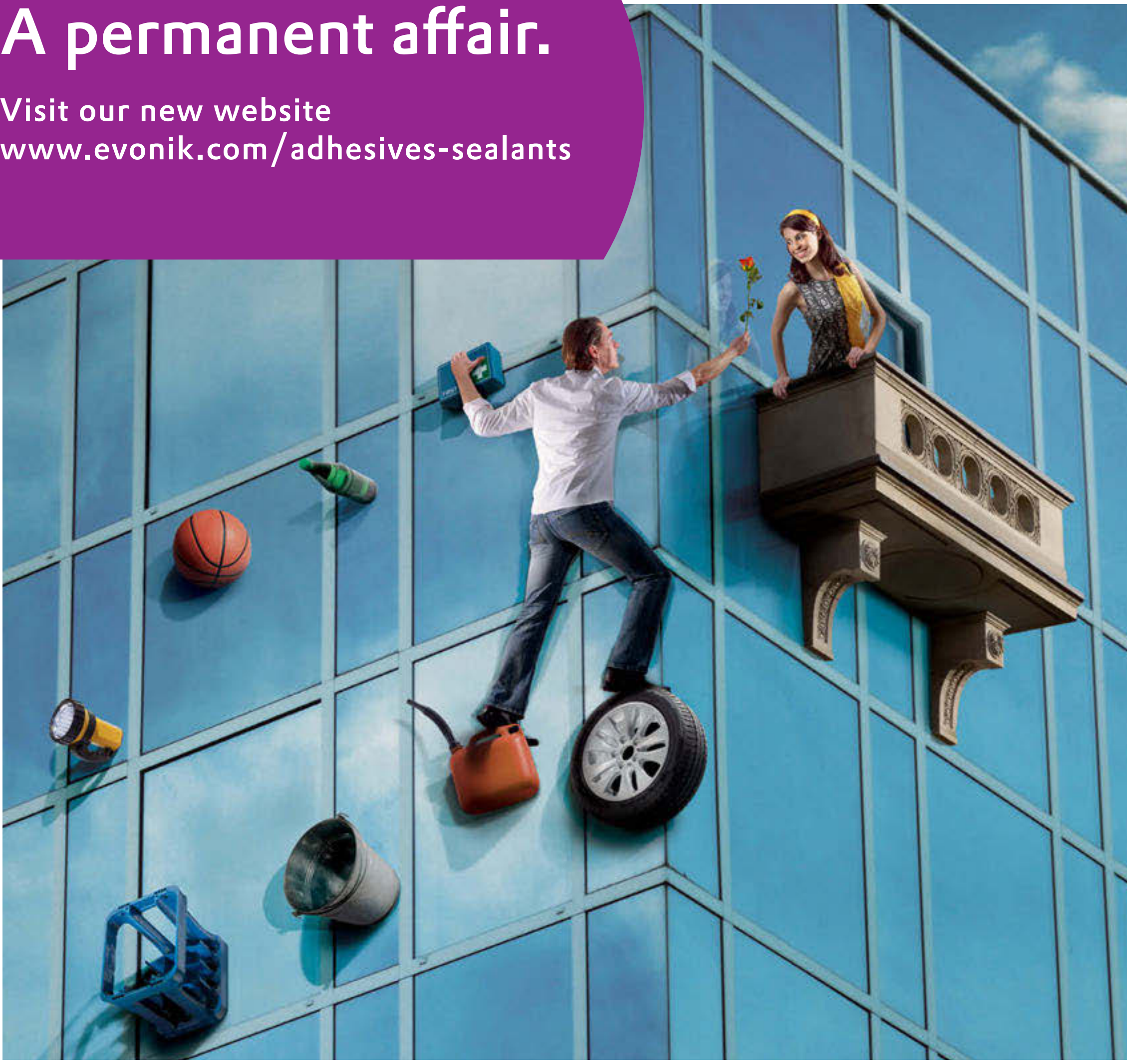


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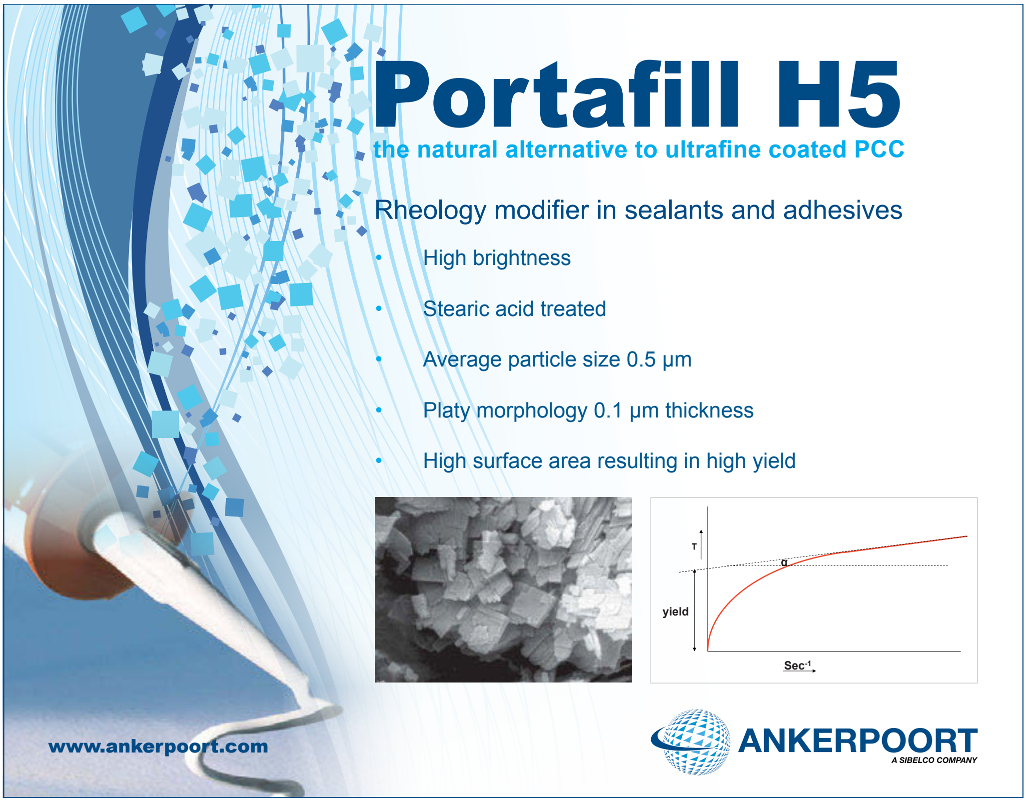

Part I General basics

1 Introduction

Nowadays, adhesive bonding is an indispensable technology for permanently joining two or more substrates in both industrial and private use. The resultant composite materials often facilitate the manufacture of innovative products [1].

In Germany alone, nearly 800,000 tons of adhesives (worth nearly 1.5 billion EUR) were consumed in 2007, and the trend is growing. Adhesives manufacturers offer more than 25,000 different products for all kinds of applications – and tailored to nearly every purpose [1].

In terms of chemical and applications technology, the field of adhesives and sealants is extremely diversified. This book can only describe the most important types; needless to say, the selection presented here is subjective.

From its title “Formulating Adhesives and Sealants” it is clear that the main focus is on the materials (chemistry) and not on the joining technology (adhesive bonding and sealing). The underlying technological aspects are both multidisciplinary and interdisciplinary by nature. Figure I-1.1 illustrates this interdisciplinarity from the point of view of adhesion (see Chapter I-2).

Figure I-1.2 illustrates this interdisciplinarity or complexity based on the factors influencing the strength of an adhesive bond.

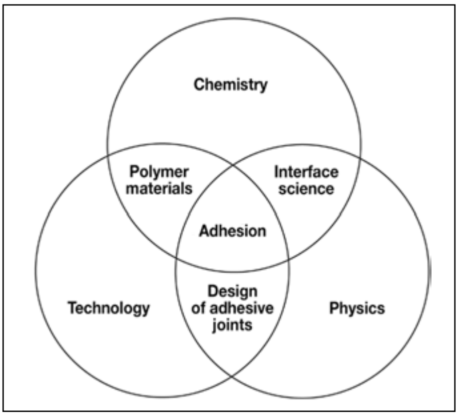

Figure I-1.1: Interdisciplinarity

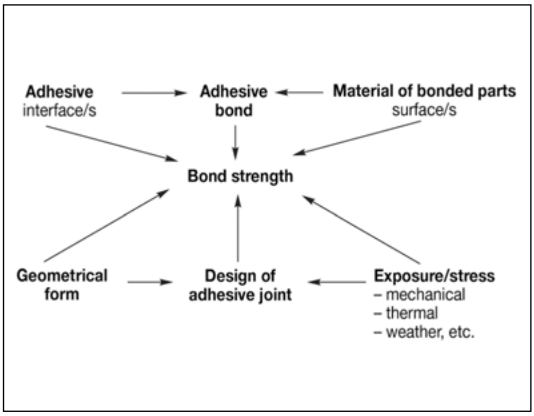

Figure I-1.2: Factors influencing the strength of an adhesive bond

1.1 Definitions

Adhesives

An adhesive is a non-metallic material which can join substrates by adhesion and cohesion [3]. Adhesives are applied in a liquid-like state, wet the substrates and then set physically or chemically (i.e. solidify).

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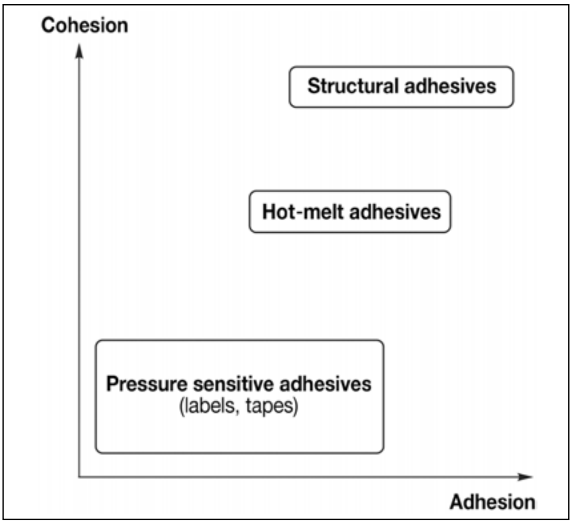

Figure I-1.3: Simplified classification of some adhesives with respect to adhesion and cohesion

Adhesives transmit loads between the bonded substrates (adherends); force-fit bonds of the kind yielded by other joining technologies, e.g. welding, brazing, and riveting, are obtained. Adhesive bonds distribute loads more uniformly over the entire joint area. This more uniform distribution of forces allows the material thickness to be used up to its maximum load-bearing capacity, facilitating the use of thinner and lighter components.

Adhesion is the attraction between a solid interface and a second phase (two different substances) whereas cohesion is the force that holds materials together. Thus, cohesion is a special form of adhesion, in which homogeneous particles adhere to each other.

Adhesive bonding denotes the joining of the same or different materials by means of an adhesive[3].

Structural adhesive bonding is the use of adhesive bonding to create a durable construction of high stability and rigidity; such adhesive bonds are characterised by high adhesion and cohesion (Figure I-1.3).

An adhesive joint is the gap between two glued surfaces which is filled by a layer of adhesive.

Sealants

A sealant is a substance for filling joints and gaps (this includes solid materials, such as rubber profiles). A joint sealant is a sealant which is introduced into a joint in a liquid-like state. A joint is a gap between structural elements that is either deliberate or required by tolerances; as a rule, a sealed joint is generally much larger than an adhesive joint; sealants are therefore gap-filling.

In practice, though, sealant is the predominant term employed. For the purposes of this book, sealants are paste materials which solidify in joints to yield more or less solid materials. The function of sealants is to fill gaps created by the assembly of structural elements made of similar or different materials, and to seal these joints so as to exclude:

- gases
- liquids
- solids (e.g. dust)
- energy loss
- noise.

Further requirements are to provide a flexible support (e.g. for glass panes on metal) or to prevent corrosion where metals are in direct contact. Moreover, a sealant must possess adequate adhesion (like an adhesive) and cohesion for the job at hand.

Solid sealants transmit only small loads between the sealed structural elements (mostly less than 1 MPa). The functionality of a solid sealant is greatly affected by its resilience (elastic recovery)[6]. In the ideal case, the resilience should be 100 %; in practice, though, it is somewhat lower. Thus, a solid seal exhibits a degree of plasticity in addition to elasticity. In particular cases, plasticity may even be desirable.

Adhesive-sealants

The transition from high to low load transfer is smooth. The technologically very important transition region between pure adhesives and pure sealants is bridged by so-called adhesive-sealants. Figure I-1.4 schematically illustrates the differences between adhesives, adhesive-sealants and sealants on the basis of stress-strain characteristics.

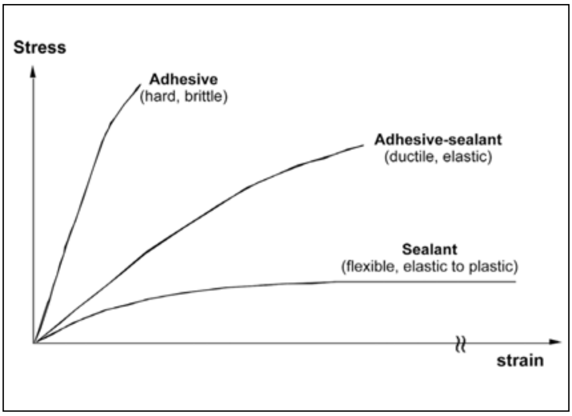

Figure I-1.4: Qualitative stress-strain characteristics of adhesives, adhesive-sealants and sealants

A second classification criterion is that of gap-filling ability. Sealants can fill gaps (up to several cm), whereas adhesives cannot (adhesive joints ≤ 1 mm). Adhesive-sealants occupy an intermediate position again, and can fill gaps up to about 5 mm wide. Figure I-1.5 illustrates the differences between adhesives, adhesive-sealants and sealants. More information on classification schemes for adhesives and sealants is presented in Chapter I-3.

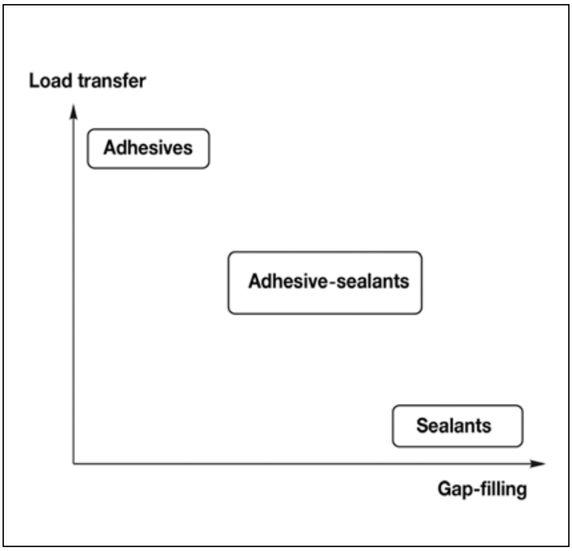

Figure I-1.5: Qualitative classification of adhesives, adhesive-sealants and sealants

Advantages of adhesive bonding [5]:

+ uniform stress distribution over the entire bonded surface,
+ no thermal influence on the microstructure of metal alloys (as is the case for welding),
+ no thermally induced distortion of structural parts,
+ bonding of different materials (e.g. glass-metal),
+ no contact corrosion (when joining electrochemically different metals),
+ joining of very thin parts (e.g. sheets),
+ joining of thermosensitive materials,
+ weight savings relative to other joining technologies,
+ combinable with screwing, riveting and spot-welding.

Disadvantages of adhesive bonding [5]:

- limited scope for repair and recycling,
- limited thermal resistance of bonded joints,
- tendency to creep,
- extensive quality control and quality assurance measures needed,
- ageing of organic adhesive layers (e.g. autoxidation),
- process parameters must be closely observed.

1.2 Setting of adhesives and sealants

For application, adhesives and sealants must be flowable so that they can wet the substrates; this is a requirement for adhesion (Chapter I-2). Setting by adhesives and sealants is also called solidification and represents the transition from the flowable to the solid state. This transition can occur purely physically or by chemical reaction. Figure I-1.6 schematically shows the most important setting mechanisms.

An exception here are pressure sensitive adhesives, which are permanently tacky (e.g. for labels or adhesive tapes) and which, strictly speaking, do not solidify. Pressure sensitive adhesives are applied as solutions, aqueous dispersions or melts (all of which set physically) and even as reactive UV-curing systems (see Chapter II-3.5) thus, they extend beyond the scope of Figure I-1.6.

Physical setting

The binder polymers already exist prior to physical setting [3]. They are rendered flowable by dissolving or dispersing them in solvents (including water). Setting occurs by solvent evaporation; compare the physical drying of paints [4]. Another possibility is to melt thermoplastic polymers; this is a reversible process. Contact adhesives set by partial crystallisation of the polymers. The special setting process undergone by plastisols is described in detail in Chapter III-1.2.1.

All physically setting adhesives and sealants are plastomers (see Figures I-1.7 and I-1.8) and have disadvantages, such as poor solvent resistance and heat distortion.

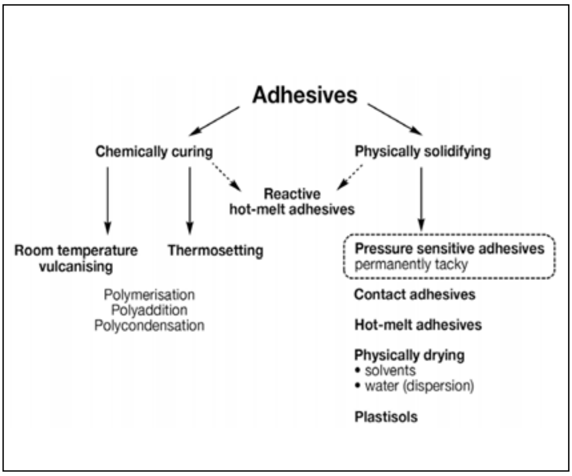

Figure I-1.6: Classification of adhesives by (the most important) setting mechanisms

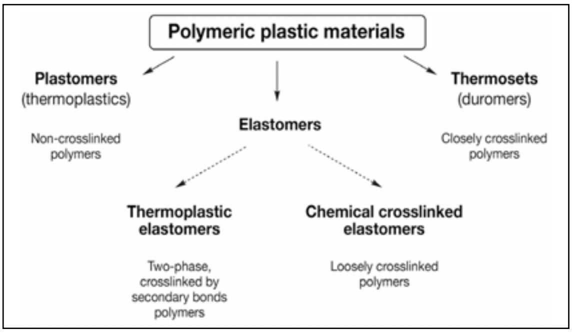

Figure I-1.7: Classification of polymeric plastic materials

Chemical setting

The binders of chemically setting (curing) adhesives and sealants are flowable monomers or prepolymers (oligomers). Like chemically curing coatings [4], chemical setting in adhesives and sealants is marked by an increase in molecular mass and more or less pronounced crosslinking. The crosslink density dictates whether thermosets or chemically crosslinked elastomers are formed (see following section).

Organic binders for adhesives and sealants as polymeric materials

Here, adhesives and sealants will be considered from the point of view of plastics technology. Basically, organic binders in solid adhesives and sealants are nothing other than polymeric plastics and could be classified in the same way (Figures I-1.7 and I-1.8) [4].

Physical drying of polymer solutions and dispersions or cooling of polymer melts yields plastomers. Chemical reaction (curing) leads to either thermosets or chemically crosslinked elastomers, in accordance with the crosslink density.

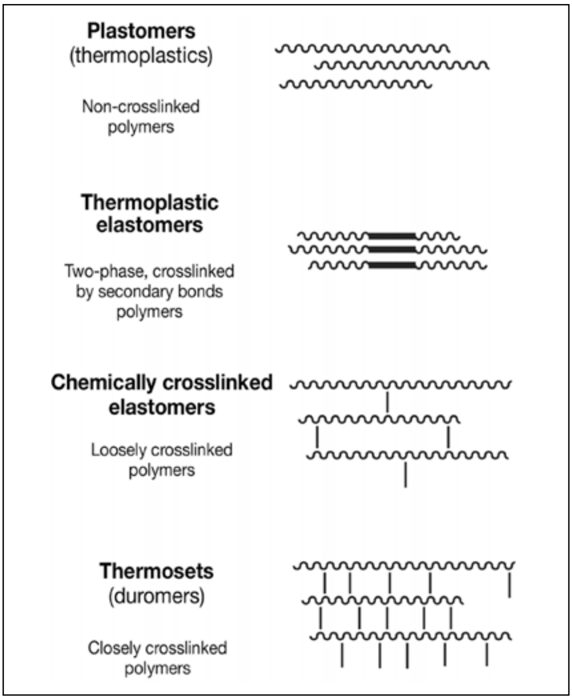

Figure I-1.8: Simplified diagram of polymeric plastic materials

One exception is thermoplastic elastomers, which are applied as a melt but exhibit elasticity at room temperature because of secondary valence bonds (see Chapter II-1.3 and III-2.2.2.3). All the different types of polymer materials presented in Figures I-1.7 and I-1.8 are used in adhesives and sealants and will be described as specific examples in the course of this book.

The term elasticity is very important with respect to adhesives and sealants. Elasticity is a property by which solid matter returns to its original state after deformation (recovery). Figure I-1.9 schematically shows entropy elasticity (rubber-like elasticity), which is observed especially in polymers. Entropy elasticity is caused by the tendency of polymers to assume a disordered conformation (of high entropy). Figure I-1.10 clearly shows the elasticity, and especially the recovery, of a cured polysulphide construction sealant (Chapter III-3.2.2). Application of force causes distortion of the sealant (Figure I-1.10, right); when the force is removed, the sealant returns to its original state (Figure I-1.10, left).

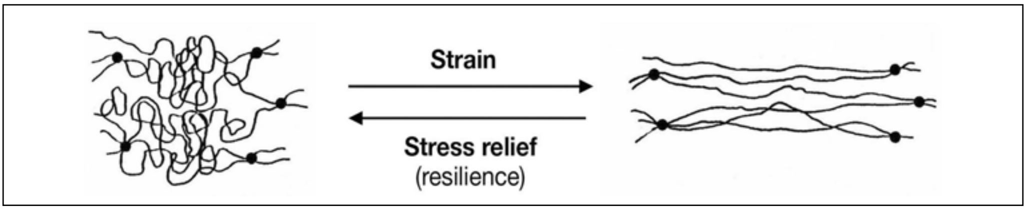

Figure I-1.9: Simplified diagram of entropy elasticity or rubber-like elasticity

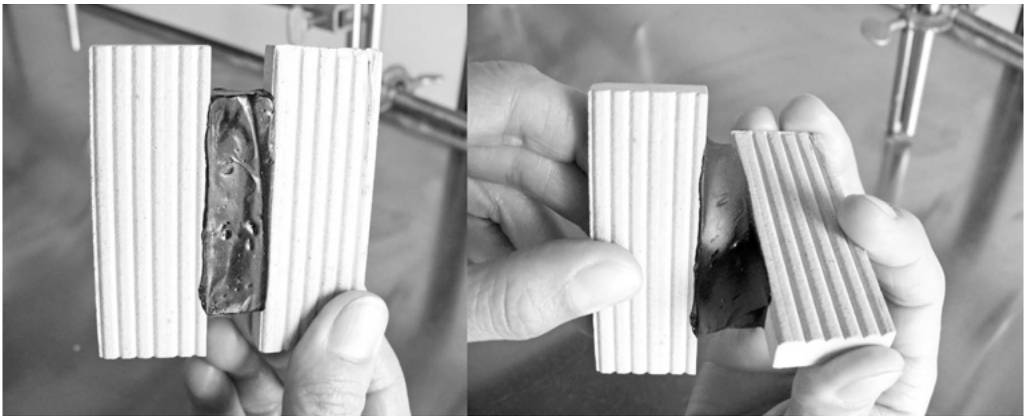

Figure I-1.10: Test specimen with cured polysulphide construction sealant, with (right) and without (left) application of force

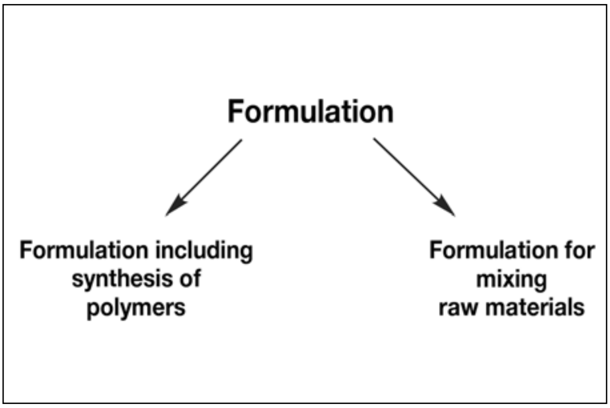

Figure I-1.11: Formulation of adhesives and sealants

Paint formulating[4] often entails the mixing of commercially available raw materials, whereas the formulation of adhesives and sealants may also include the synthesis of polymers (Figure I-1.11). Examples are adhesive-sealants for bonding windscreens to car bodies (Chapter III-1.3) where so-called "one-shot processes" are employed. These consist in simultaneous mixing of the ingredients, dispersion of the fillers and production of an isocyanate-terminated prepolymer.

As in coatings, an emerging trend in adhesives is the incorporation of nanoscale, surface-modified (and therefore reinforcing) fillers to improve mechanical properties[13].

1.3 Commercial importance

Adhesives

Global demand for adhesives in 2007 was estimated at 11 million tons. A regional breakdown of consumption is presented in Figure I-1.12.

The various application areas for adhesives are presented in Figure I-1.13[8]. The bulk of adhesives is consumed by the paper and packaging industry (Figure I-1.13); most packaging is a short-lived mass-produced article[8]. As in paints and coatings[4], construction applications are very important.

The various application forms for adhesives are presented in Figure I-1.14[9]. While aqueous systems predominate in adhesives, just as in paints and coatings[4], emissions-free and recyclable hot-melt adhesives (Chapter II-1.3) are of great economic importance (Figure I-1.14). Solvent-based systems are declining in importance for the familiar ecological reasons.

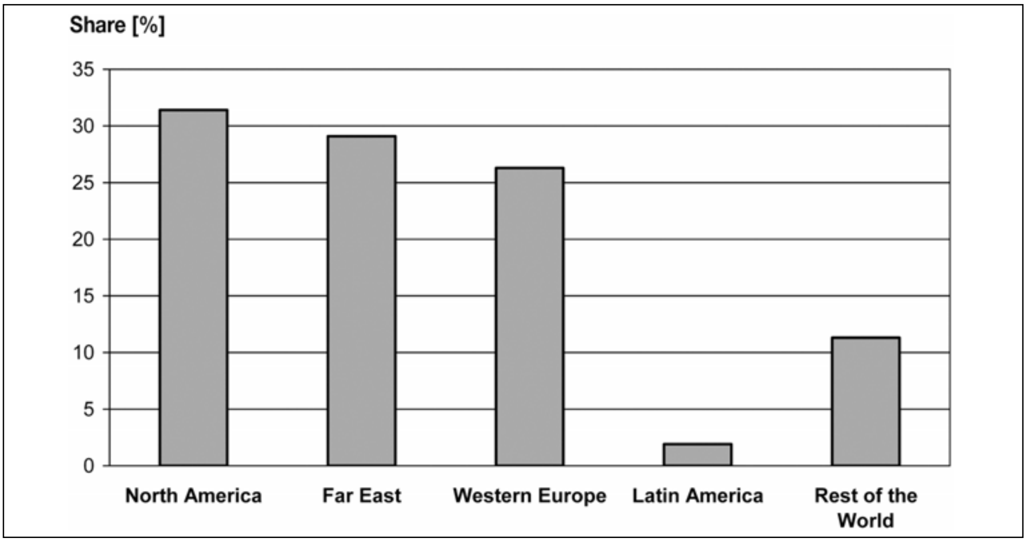

Figure I-1.12: Regional breakdown of demand for adhesives and sealants in 2007 (100 % equates to 11 million tons)[7]

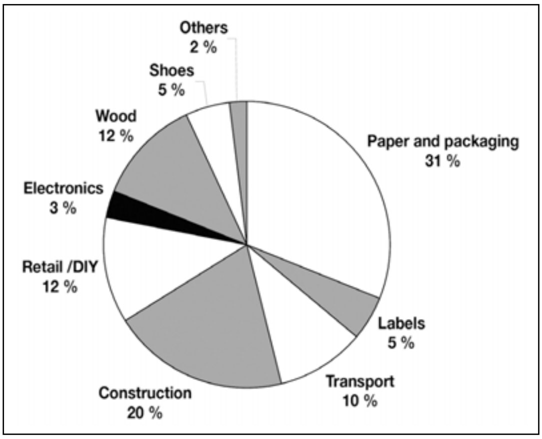

Figure I-1.13: European adhesives market

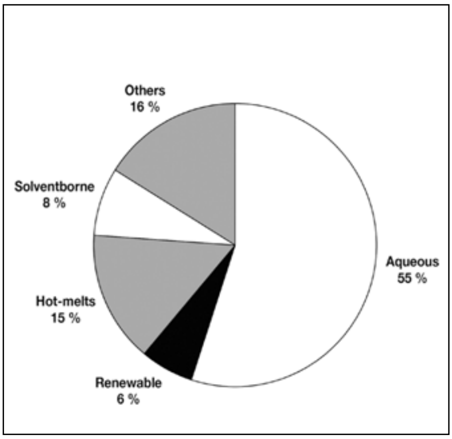

Figure I-1.14: Application forms for adhesives (renewable means based on renewable raw materials)

Sealants

A regional breakdown of the various application areas for sealants is presented in Figure I-1.15.

The various applications for sealants are presented in Figure I-1.16 [11], and are predominantly in the area of construction [including glazing, insulating glass (IGS) and do-it-yourself (DIY)]. The various base materials for the most important sealant systems are shown in Figure I-1.17 (regional breakdown) [10].

Silicones predominate here because they are mainly used in construction (see Figure I-1.16). All the various types of sealants presented in Figure I-1.17 will be described in the course of this book.

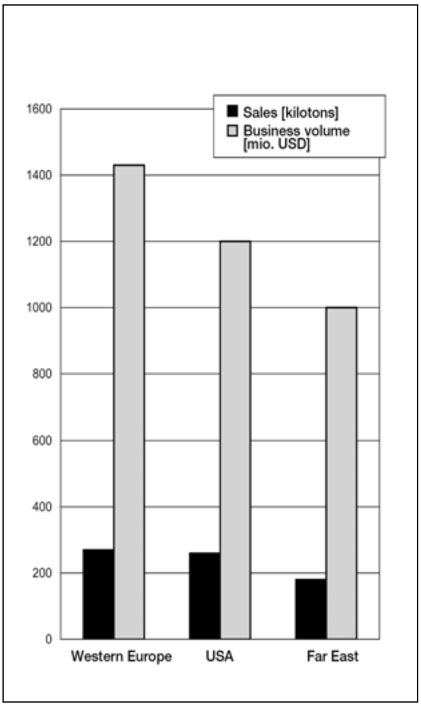

Figure I-1.15: Regional breakdown of sealants consumption

Base materials

The different base materials for adhesives and sealants are recorded in Figure I-1.18 [12]; this shows how multifaceted the chemistry of adhesives and sealants is. It should be emphasized that not all types of adhesives and sealants in Figure I-1.18 can be described in this

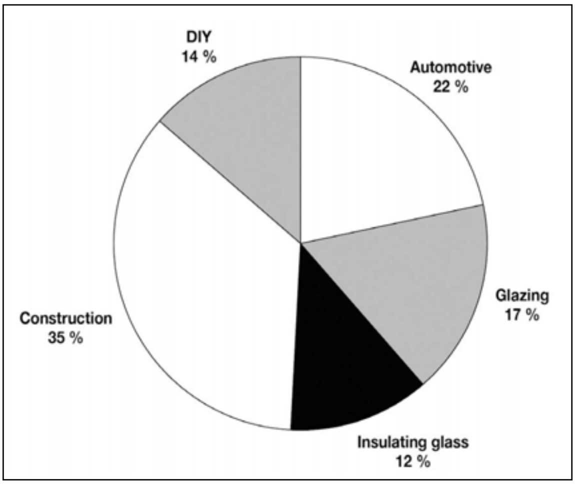

Figure I-1.16: End-user market for elastic sealants in Europe

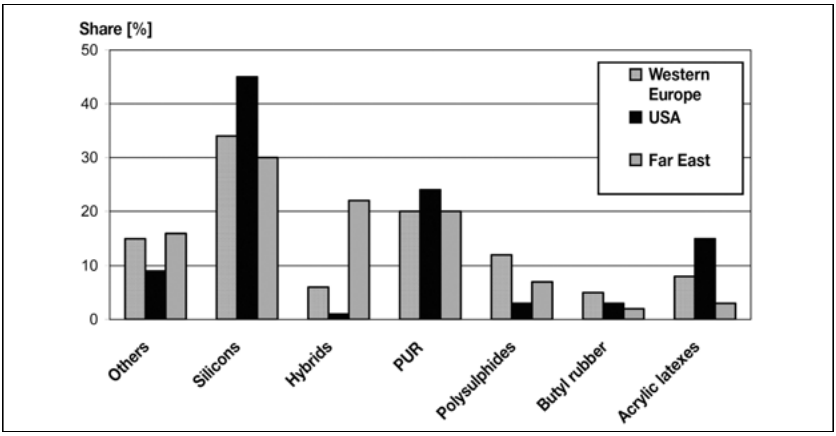

Figure I-1.17: Base materials for sealants (regional breakdown)

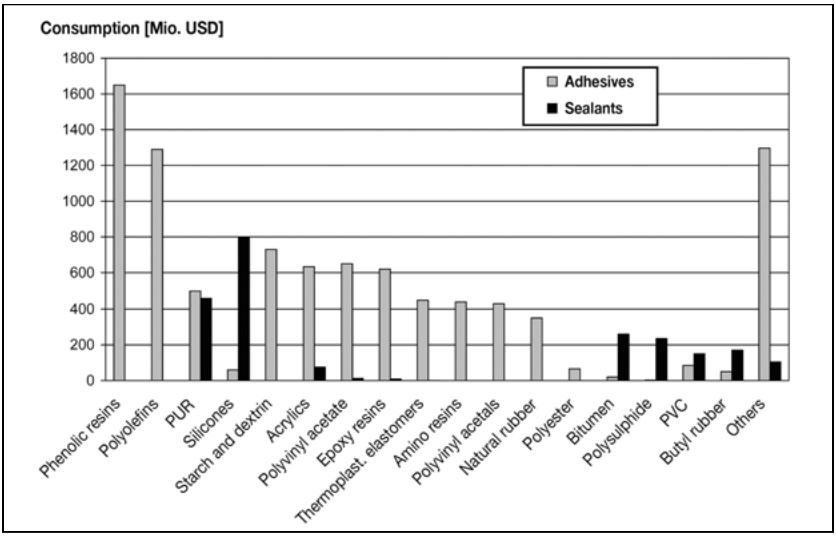

Figure I-1.18: Consumption of adhesives and sealants by base raw material in the USA (1998)

book. As this book focuses on premium adhesives and sealants, those binders which are based on amino resins and, to some extent, phenolic resins are not discussed, as they are used in chipboard (high quality phenolic resins, see Chapter II-2.4). Nor will low-quality, bituminous sealants be described.

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2 Adhesion

Adhesive strength is a measure of the resistance of an adhesive bond to mechanical removal from a substrate (for tensile load it is given by force/area: MPa or N/mm^2; but for peel strength it is given by force/length: N/mm). In the following, we talk about adhesives; however, similar considerations apply to sealants and – as described earlier [1] – to coatings.

2.1 Wetting of substrates

A prerequisite for good adhesion (albeit insufficient on its own) is adequate wetting of the solid substrate by the liquid adhesive during application. The substrate/air interface (surface) is converted to a substrate/liquid interface. Subsequent setting of the adhesive yields a substrate/solid interface. It should be noted that it is difficult to define the solidification state of adhesives. For example, permanently tacky pressure sensitive adhesives on labels are always in the state of a high-viscosity liquid.

Surface and interfacial tension

In a liquid, such as water, all molecules in the bulk phase are uniformly surrounded by their neighbouring molecules. Thus, the attractive forces acting on these molecules extend equally in every direction in space and cancel each other out (Figure I-2.1). At the water/air interface, things change dramatically because a water molecule there is surrounded only in the interface itself and in the direction of the bulk phase. Thus, the forces of attraction do not cancel each other out; a force acts on the water molecule towards the inner phase of the liquid (Figure I-2.1). This force causes the liquid's surface to become as small as possible. That is why a droplet in outer space is spherical – the sphere has minimal surface area combined with maximum volume.

This force has to be quantified. The interfacial tension (γ) is a force acting along 1 m of an imaginary boundary between two phases [force/length = N/m; mostly quoted in mN/m, formerly in dyn/cm]. If one of the phases is air, the tension is called the surface tension.

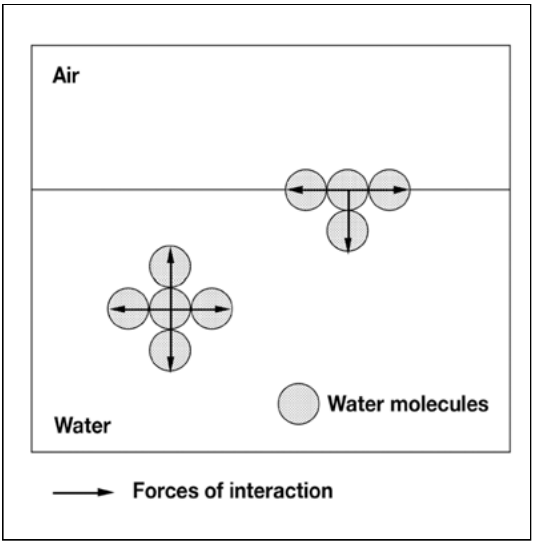

Figure I-2.1: Force diagram to explain surface tension

For the surface area of a liquid to increase, molecules must move from the bulk to the surface. This means that forces of attraction must be overcome, work done and energy expended.

The following mathematical derivation shows how energy/area is equal to force/length. In other words, surface tension is also a measure of surface energy:

$$\frac{\text{Energy}}{\text{Area}} = \frac{\text{J}}{\text{m}^2} = \frac{\text{N} \cdot \text{m}}{\text{m}^2} = \frac{\text{N}}{\text{m}} = \frac{\text{Force}}{\text{Length}}$$

interfacial or surface tension

Typical surface tensions of liquids are presented in Table I-2.1.

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Table I-2.1: Surface tension [mN/m] of liquids (these values may vary slightly from one literature reference to another)

Mercury	500 1)
Water	73
Epoxy resins	45 to 60
Melamine resins	42 to 58
Alkyd resins	33 to 60
Acrylic resins	32 to 40
Butyl glycol	32
Xylene	29 to 30
White spirit	26 to 27
Butyl acetate	25
Butanol	23
White spirit	18 to 22 2)
Hexane	18

1) liquid metal
2) free of aromatic hydrocarbons

The greater the surface tension, the greater is the cohesion in the respective liquid phase and the stronger are the forces of interaction between the atoms or molecules in that phase. Water molecules associate strongly with each other by means of hydrogen bonds, which generate a high level of cohesion and a high surface tension. The water surface behaves like a skin. The less polar a liquid is, the lower is its surface tension.

Wetting

A simplified diagram of the wetting of a solid surface (substrate) by a liquid is presented in Figure I-2.2.

A measure of wetting is provided by the contact angle Θ formed between the solid substrate and the liquid drop (Figure I-2.2). The smaller the contact angle Θ, the better is the wetting.

Mathematically, wetting is described by Young's equation:

$$\gamma_S = \gamma_{SL} + \gamma_L \cdot \cos\Theta$$

Complete wetting of a substrate by a liquid is called spreading: $\Theta = 0°$ and $\cos\Theta = 1$.

For spreading, Young's equation becomes $\gamma_S = \gamma_{SL} + \gamma_L$ and $\gamma_L = \gamma_S - \gamma_{SL}$. A liquid, such as an adhesive, cannot wet the surface of a solid substrate unless its surface tension is lower than that of the substrate ($\gamma_L < \gamma_S$). Thus, if a liquid has a higher surface tension than the substrate, there will be no wetting.

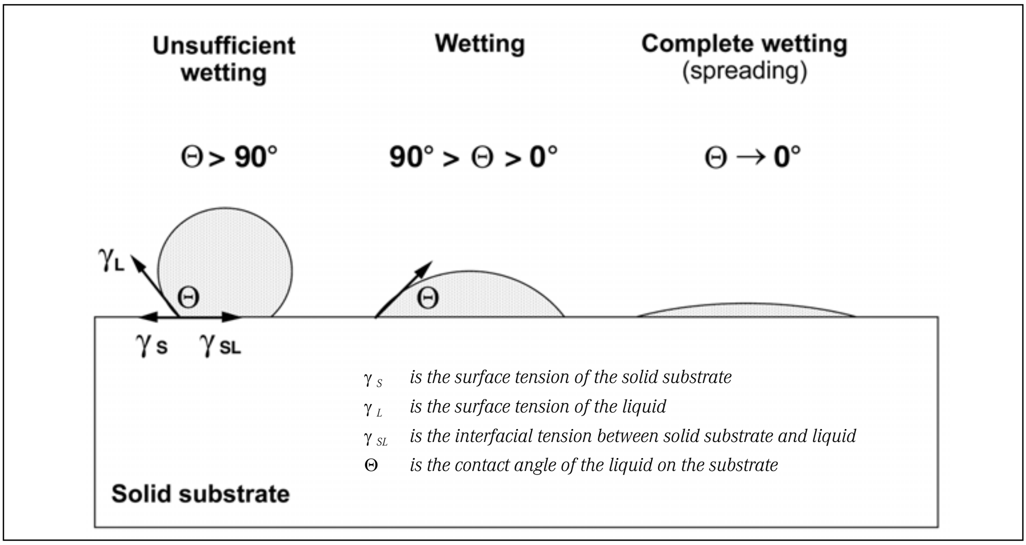

Figure I-2.2: Wetting of a solid substrate by a liquid

The surface tensions of metals that are quoted in the literature range from several hundred to several thousand mN/m (see mercury in Table I-2.1); these values refer to liquid metals at their melting temperatures[17]. Where wetting is concerned, it is the surface tension (at ambient temperature) of solid metal surfaces covered by oxide and layers of adsorbed substances which is important (Table I-2.2). The critical surface tension of solids (glass, metal, plastics in Table I-2.2) can be measured indirectly by wetting experiments (measurement of contact angles, Zisman method)[14, 16, 17].

Allowance must be made for possible changes in the surfaces of substrates (e.g. oxide layers, mould-release agents) as these may greatly affect the surface tension (see Table I-2.3).

Table I-2.2: Critical surface tension of solid substrates [mN/m]

Glass	73
Phosphated steel *	43 to 46
Poly(vinyl chloride)	39 to 42
Tin-plated steel *	approx. 35
Aluminium *	33 to 35
Polyethylene	32 to 39
Polypropylene	28 to 29
Steel (untreated) *	29
Polydimethylsiloxane	19**
Polytetrafluorethylene	19

** Solid metal (oxide) surfaces! Melted (liquid) metals have much higher surface tensions (see mercury in Table I-2.1). These values may vary slightly in the literature.*
*** silicones up to 24*

Table I-2.3: Contact angle for water on various aluminium surfaces

Aluminium surface	**Contact angle Θ (± 5°)**
rolled	63
pickled with a commercial caustic	22
pickled with NaOH	31

Metal surfaces

If the prerequisite for wetting is $\gamma_L<\gamma_S$, then water theoretically should not spread over metal surfaces (see relative low surface tensions of solid metals, Table I-2.2). This is borne out by measurements of the contact angles for water on various pretreated aluminium sheets (Table I-2.3); the water wets ($\Theta < 90°$), but it does not spread ($\Theta > 0°$).

Figure I-2.3 is a schematic diagram of an aluminium surface[2] that is better described as an aluminium oxide surface; similar considerations apply to the surfaces of all commonly employed metals. If the model presented in Figure I-2.3 reflects reality, the hydrated aluminium oxide surface would be completely wetted by water; but this is not observed (Table I-2.3). Figure I-2.3 is a simplification of the real situation. ESCA/XPS measurements show that variously pretreated aluminium surfaces contain a significant amount of carbon in addition to aluminium and oxygen. Presumably, carbon is adsorbed from the air (e.g. carbon dioxide or hydrocarbons)[3, 6]; see also Chapter I-2.3.2.2 (Figure I-2.21). Thus, while there is still no universal model that describes the structure of metal surfaces, metal oxides are certainly present.

Surfaces of plastics

Even more complicated are the surface structures of engineering plastics[2]. The problem here is that the bulk properties of the polymer are different from those of the surface. These differences may be due to the composition of the plastic or to the production or processing conditions. Mostly, their surfaces have low energies (low surface tension), which leads to poor wetting.

Composition of plastics

Many plastics contain low-molecular components, such as additives (e.g. stabilisers), solvent residues and sometimes plasticisers. All these components can impair adhesion if they are

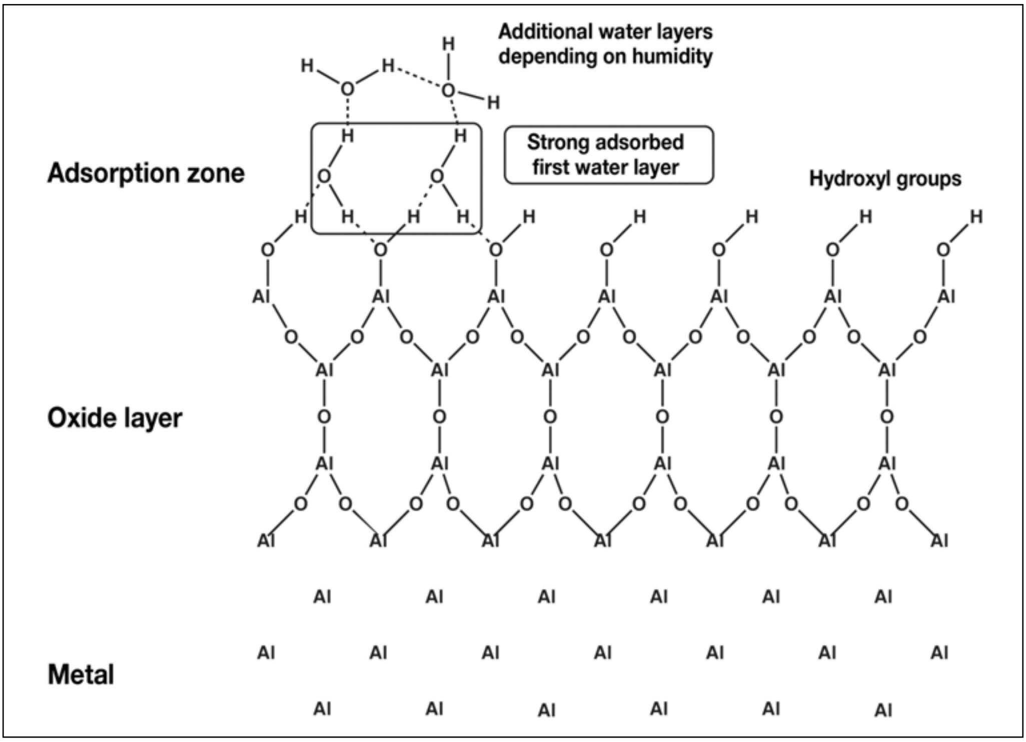

Figure I-2.3: Hydrated aluminium (oxide) surface (simplified model)
Similar considerations apply to the Fe/Fe$_2$O$_3$ system

present on the surface. Many low-molecular components tend to migrate to the surface and accumulate there. Thus, plastics may have an anti-adhesive layer on the surface (Figure I-2.4).

Production and processing conditions of plastics

a) Mould-release agents

When injection-moulded or compression-moulded plastic parts have to be released from the mould, internal and external mould-release agents are used. Internal mould-release agents are mixed into the plastic pellets and are distributed throughout the plastic material; therefore, sanding the plastic surface is useless. Internal mould-release agents generate plastic surfaces that are barely if at all wettable. External mould-release agents, in contrast, are sprayed into the open injection mould; they are based on paraffins, soaps and oils (including silicone oils). Because of the processing conditions, external mould-release agents are subsequently found not only in the surface layer, but also in the underlying layers.

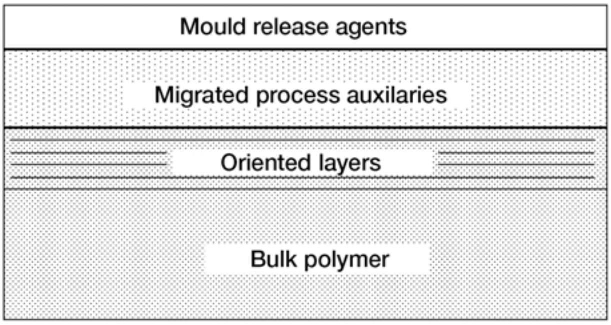

Figure I-2.4: Surfaces of engineering plastics

b) Surface properties caused by processing conditions

Injection and compression moulding create surface properties that differ from those of the bulk polymer. The dense surface layers of moulded plastic materials are very smooth (orientated layers; Figure I-2.4).

Improvement in wetting

In the case of water-based adhesives especially $\gamma_L > \gamma_S$ leads to poor wetting. There are two ways to improve wetting:

- Lower the surface tension of the water-based adhesive (γ_L) by adding wetting agents (see [1]).
- Increase the surface tension of the substrate (γ_S).

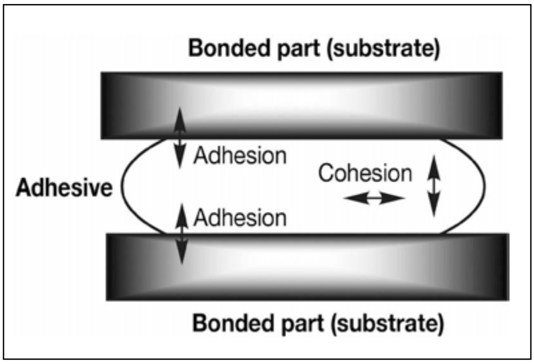

Figure I-2.5: Adhesive bond

For example, the surface tension of metals is increased by phosphating (see Table I-2.2). Oxidation of plastic surfaces (e.g. by flame treatment) generates polar functional groups (e.g. -OH, -COOH) on the surface and increases γ_S. A detailed description of pretreatment processes for various plastics is provided in [2, 10, 15]. Sometimes the wettability of plastic surfaces can be improved by sanding or rubbing with emery paper or cleaning with organic solvents or water-based cleaners.

Furthermore, primers may be applied first to improve bonding. For example, polyolefins (low surface tension, Table I-2.2) can be coated with chlorinated polymers, which increase the surface tension [2].

2.2 Adhesion forces and mechanisms

So far, no universal theory of adhesion exists, and those theories which do exist explain only aspects of it. Nonetheless, a partial theoretical explanation of phenomena related to adhesion is better than none.

Adhesion/cohesion

Adhesives and sealants must exhibit sufficient adhesion to the joined substrates (as well as sufficient cohesion).

Adhesion is the attraction which exists at the interface of two different solid phases. Adhesion is expressed in units of energy/area (compare surface tension); in contrast, the units of adhesive strength are force/area.

The counterpart to adhesion is cohesion. Cohesion is the attraction which exists within a single phase (in the solidified adhesive or sealant phase). Cohesion is a state in which particles (molecules) of a single substance are held together; it is a special instance of adhesion in which only molecules of the same kind adhere to each other. Figure I-2.5 explains adhesion and cohesion in an adhesive bond.

Modes of adhesive bond failure

Loss of adhesion by a bond yields the following failure modes, the extent of which varies with the level of adhesion and cohesion.

Adhesive failure:	adhesion < cohesion	
Cohesive failure:	adhesion > cohesion	(desired)
Both types of failure:	adhesion ≈ cohesion	
Failure of the substrate:	adhesion and cohesion > strength of the substrate	(rare)

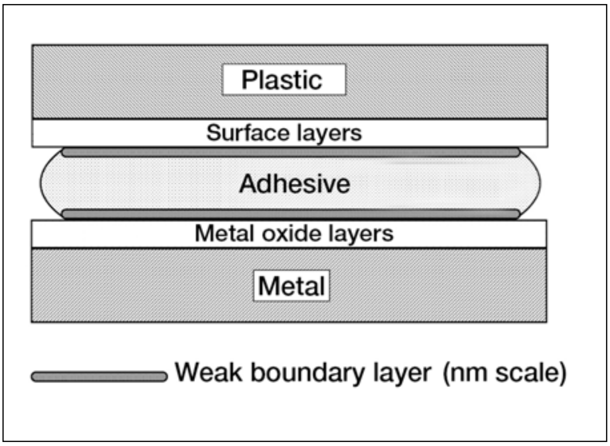

Figure I-2.6: Adhesive bond between a plastic and a metal part (simplified)

It should be pointed out that much adhesive failure is often unrecognized cohesive failure within a weak layer of adhesive close to the interface (weak boundary layer; Figure I-2.6). The chemical composition of the adhesive or the arrangement of the polymer molecules in the boundary layer often differs from that in the bulk materials. For example, a zone of reduced strength can be formed between the chemisorbed polymer on the substrate (monolayer) and the bulk polymer. For simplicity, this unwanted failure mode is usually called adhesive failure, too.

Figure I-2.7: Adhesive failure (left) of a sealant in an expansion joint

Weak layers of adhesive close to an interface are also observed in plastic substrates (polymer materials; see Figure I-2.4) and on metals (certain oxide layers; see Figure I-2.6) [2].

Figure I-2.7 shows an example of adhesive failure; clearly, loss of adhesion causes the solidified sealant in an expansion joint to lose its sealing ability.

Theories of adhesion

In general, a distinction is made between specific adhesion (interaction of interfaces irrespective of the geometrical form of the surface) and mechanical adhesion (Figure I-2.8). Mechanical adhesion (Figure I-2.9) takes place when liquid adhesive enters into cavities (voids, roughness) of the substrate and the cured adhesive is anchored mechanically therein. Prerequisites for efficient mechanical adhesion are adequate wetting of the substrate by the adhesive and a low adhesive viscosity.

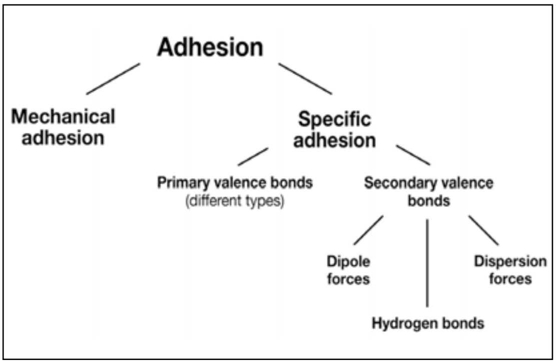

Figure I-2.8: Mechanisms of adhesion

A consequence of Table I-2.4 is that optimal adhesion is the result of primary valence bonds between adhesive and substrate. Primary valence bonds will therefore be discussed first.

Ionic bonds

Ionic bonds (e.g. salt formation) are formed especially on mineral substrates, such as metal oxide layers, phosphated metal surfaces and so on (Figures I-2.10 and I-2.11).