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.

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).
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.

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.

Advantages of adhesive bonding:

+ 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:

- 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[8]. 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.

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.
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).
Paint formulating\textsuperscript{[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\textsuperscript{[13]}.

\subsection*{1.3 Commercial importance}

\textbf{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\textsuperscript{[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\textsuperscript{[8]}. As in paints and coatings\textsuperscript{[4]}, construction applications are very important.

The various application forms for adhesives are presented in Figure I-1.14\textsuperscript{[9]}. While aqueous systems predominate in adhesives, just as in paints and coatings\textsuperscript{[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.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Regional breakdown of demand for adhesives and sealants in 2007 (100 % equates to 11 million tons)\textsuperscript{[7]}}
\end{figure}
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\(^1\), 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)\(^2\).

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.

Base materials

The different base materials for adhesives and sealants are recorded in Figure I-1.18\(^3\); 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...
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.

1.4 References