WETTING AND AHESION OF LIQUIDS ON SURFACES

BENETZUNG UND ADHÄSION VON FLÜSSIGKEITEN AUF FESTKÖRPERN

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SUMMARY

Wetting is the behaviour of a liquid on contact with the surface of a solid. Wettability is the associated property of the solid surface. Depending on the liquid and the solid body material as well as the surface condition, the liquid wets more or less [1]. Whether a drop of liquid spreads on a solid surface or not depends on the surface tension of the drop and the surface energy of the solid surface. In principle, the surface energy of the solid must be higher than the surface tension of the liquid.

ZUSAMMENFASSUNG

Benetzung ist das Verhalten einer Flüssigkeit bei Kontakt mit der Oberfläche eines Festkörpers. Benetzbarkeit ist die dazugehörende Eigenschaft der Festkörperoberfläche. Je nach Flüssigkeit und je nach Festkörpermaterial sowie Oberflächenbeschaffenheit benetzt die Flüssigkeit mehr oder weniger [1]. Ob sich ein Flüssigkeitstropfen auf einer Festkörperoberfläche ausbreitet oder nicht, hängt von der Oberflächenspannung des Tropfens und von der Oberflächenenergie der Festkörperoberfläche ab. Grundsätzlich gilt für die Benetzung, dass die Oberflächenenergie des Festkörpers höher sein muss als die Oberflächenspannung der Flüssigkeit.

1. WETTING AND ADHESION

A wetting of the adherend (solid) or the wettability of the adherend with (liquid, viscous) adhesive is a prerequisite for the development of adhesion. It depends on the surface energy of the solid body, the interfacial tension between adhesive and solid body, as well as the surface tension of the liquid adhesive. If a drop of liquid is placed on a solid surface, the contact angle (edge angle) Θ is formed at the edge of the drop (Fig. 1). The surface tension of liquids σ_L and solids σ_S can be measured using various methods. For liquids, the surface tension can be measured directly; for solids, it can be measured indirectly by determining the contact angle Θ of various test liquids that are applied to the solid and whose surface tension is known [2]. The interfacial tension σ_{LS} cannot be measured. It is described by the Young equation (1).

$$\sigma_S - \sigma_{LS} = \sigma_L \cdot \cos \Theta \tag{1}$$

with

σ_S	surface energy of the solid	[mN/m]
σ_L	surface tension of the liquid	[mN/m]
σ_{LS}	interfacial tension between liquid and solid	[mN/m]
Θ	contact angle	[degree]
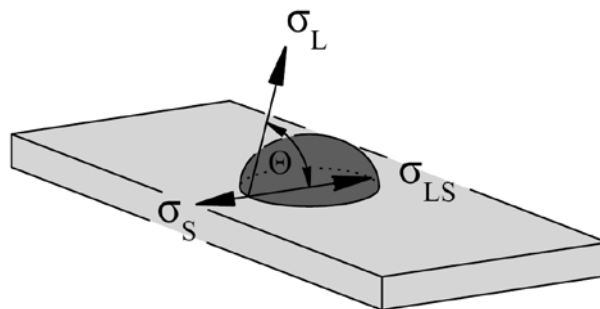
Fig. 1: Wetting of a solid body by a liquid

The contact angle Θ is a measure for the wetting behaviour and can take on values between 0° and 180° (Fig. 2). A solid is wettable if the contact angle Θ is less than 90°. Good wettability is present at an angle below 30°. When fully wetted, the contact angle is 0° and this is called spreading, i.e. the spreading of liquids over a large area on surfaces. For the stress ratios, wettability is given if the surface energy of the solid is at least equal to or greater than the surface tension of the liquid ($\sigma_S \geq \sigma_L$) [3].
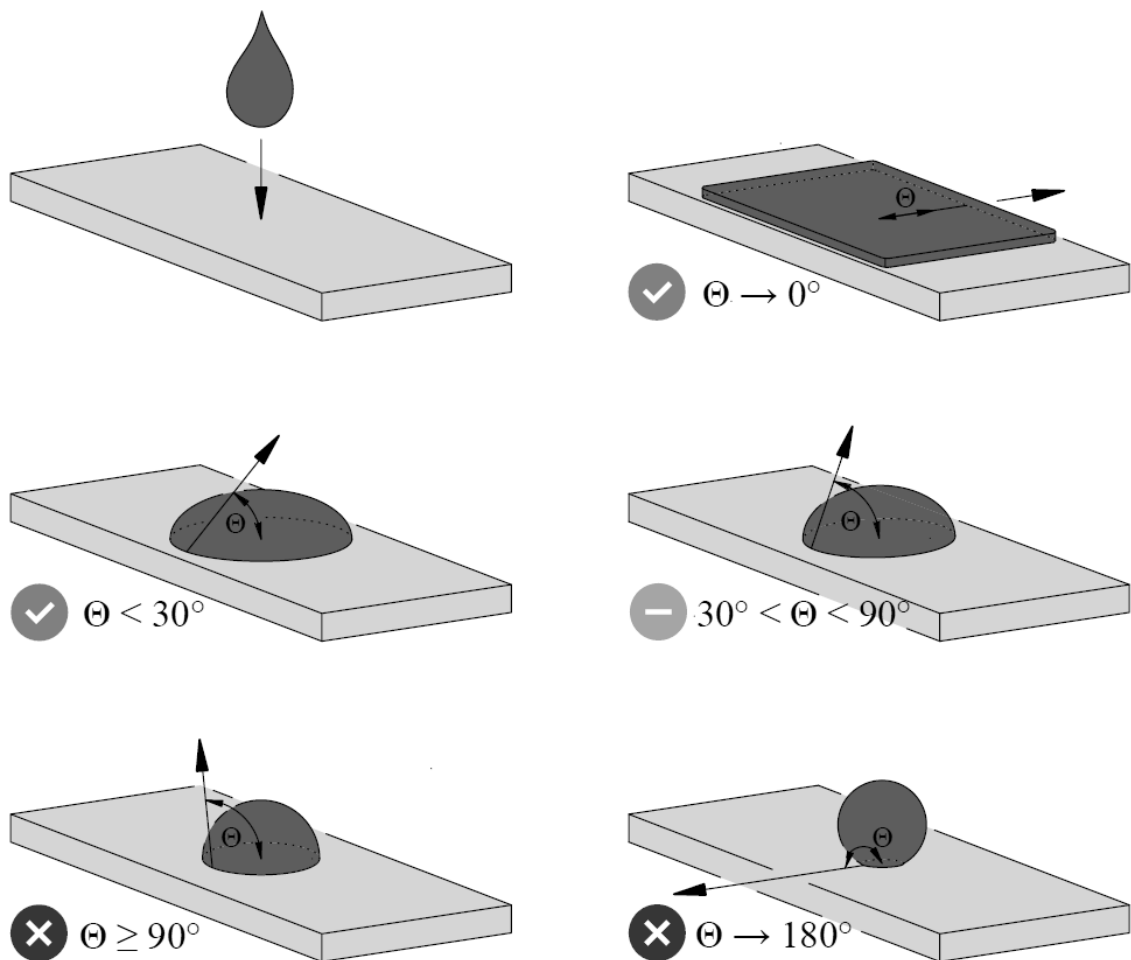

Fig. 2: Wetting angle and adhesion tendency as a function of the contact angle Θ

2. WETTING AND ADHESION WORK

The wetting behaviour of liquids is determined by the interaction of the surface forces of liquid and solid. In thermodynamic adhesion theory, the achievable adhesion is determined by the work of adhesion W_A. The work of adhesion W_A is defined as the work required to separate two substances (mixtures of substances) with a contact area of 1 cm² [3]. If the surface energies for a liquid and a solid are known, the work of adhesion W_A can be determined according to Dupré using equation (2):

$$W_A = \sigma_L + \sigma_S - \sigma_{LS} \tag{2}$$

So if a solid is wetted with a liquid, two previously existing surfaces disappear and release energy through the surface tensions σ_L and σ_S. At the same time, energy is needed to form the new interface σ_{LS}. The difference between the energy obtained and the energy consumed per unit area is the work of adhesion. If equation (1) is converted to σ_{LS} and used in equation (2), the Young-Dupré equation ((3) is obtained [3]:

$$W_A = \sigma_L \cdot (1 + \cos \Theta) \tag{3}$$

The work of adhesion assumes a maximum for $\Theta = 0°$, i.e. with complete wetting, and a minimum for the wetting angle $\Theta = 180°$ (ball). However, the work of adhesion is not a parameter for the binding forces in the boundary layer, since the energy balance only describes the wetting conditions, but not the valence bonds that form between the adhesive and the adherend. Other factors such as temperature and surface structure of the adherend also influence the wetting [3]. The calculation of the work of adhesion according to Dupré is questionable for the bonding of polymer materials, since it cannot be excluded that chemical reactions take place between the part to be joined and the adhesive during the bonding process [4].

3. SURFACE TENSION AND ADHESION

Plastics in particular have surface energies of a similar order of magnitude to adhesives. Bonding plastics with adhesives based on a similar structure is therefore problematic. However, even steels that have been pre-treated differently achieved the highest adhesive forces in tests, not at the best possible surface tension of the joined part and adhesive, but at the same surface tension [5]. This

means that even if the surface tension of the adhesive and the part to be bonded is best adjusted, the optimum results are not always achieved. Better agreement with tests and theory is achieved if the surface tension is not determined as a total value, but divided into polar and disperse fractions [6]:

$$\sigma_L = \sigma_L^p + \sigma_L^d \tag{4}$$

$$\sigma_S = \sigma_S^p + \sigma_S^d \tag{5}$$

In this case, only the polar or disperse parts of the surface tension of the part to be joined and the adhesive react with each other. The polar fractions are mainly decisive for the adhesion [5]. Polar interactions have molecules with a permanent dipole as well as the hydrogen bonds. Non-polar (disperse) forces include the dispersion forces that occur with temporary, non-permanent dipoles. The best possible adhesion is achieved when the polar components of the adhesive and the part to be joined have the same value [6, 7]. The wettability of the adherend by the adhesive is a necessary but not sufficient condition for a bond.

4. TESTS

The wetting of a material by adhesive depends on the surface tension of the liquid and the surface energy of the solid. To achieve good wetting, the surface tension of the adhesive must be lower than the surface energy of the joined part. In centric tensile tests with steel adhesives, the theory of surface tensions and their stress components were tested. For this purpose, test stamps were bonded to five different metals or metal surfaces with four different adhesives and loaded until failure (Table 1). The joint thickness of the adhesive was 0.1 to 0.3 mm.

The metals S235, 1.4401 and aluminium were used as bonding base. The material steel S235 was used in three different surface finishes, namely untreated, electro-galvanised and blasted with corundum F60. All metal surfaces, except the blasted metal surface, were cleaned with acetone before bonding. The compressed-air blasted surface was cleaned with acetone before corundum blasting and after blasting it was post-cleaned with oil-free compressed air.

Table 1: Test programme

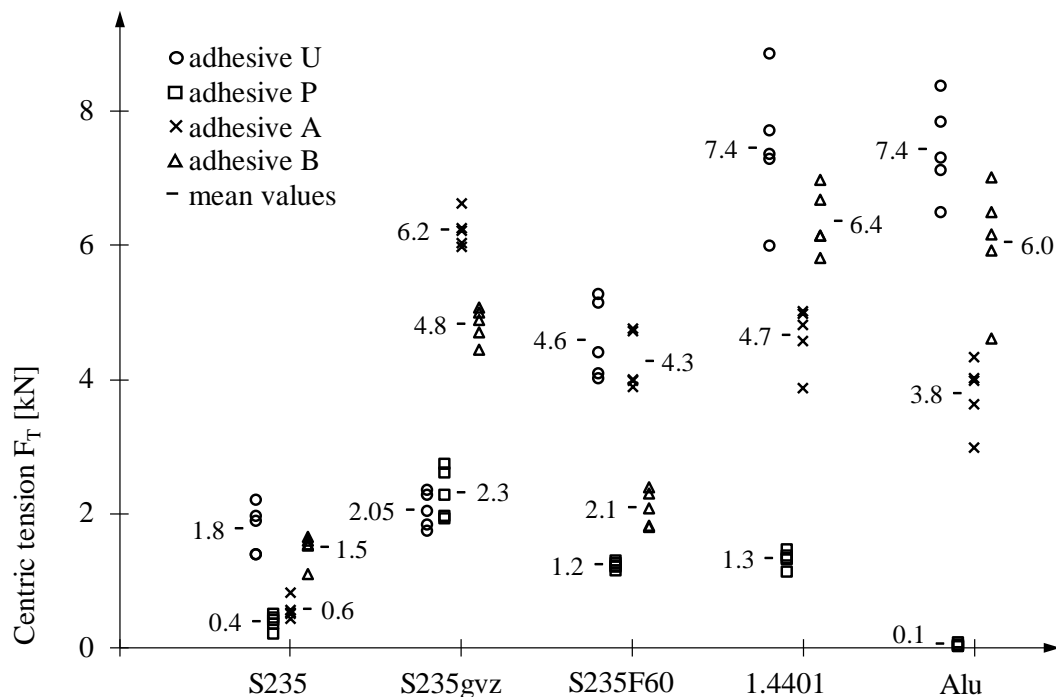| Ad-hesive	σ_L [mN/m]	$\sigma_{L\text{-disp.}}$ [mN/m]	$\sigma_{L\text{-polar}}$ [mN/m]	Adhesive base	σ_S [mN/m]	$\sigma_{L\text{-disp.}}$ [mN/m]	$\sigma_{L\text{-polar}}$ [mN/m]	Number of tests
U	37.8	37.2	0.6	S235	39.3	38.9	0.4	5
				S235gvz	37.6	34.2	3.4	5
				S235F60	47.6	45.3	2.2	5
				Alu	37.1	35.4	1.7	5
				1.4401	36.8	35.8	1.0	5
P	42.0	40.8	1.2	S235	39.3	38.9	0.4	5
				S235gvz	37.6	34.2	3.4	5
				S235F60	47.6	45.3	2.2	5
				Alu	37.1	35.4	1.7	5
				1.4401	36.8	35.8	1.0	5
A	49.4	47.8	1.6	S235	39.3	38.9	0.4	5
				S235gvz	37.6	34.2	3.4	5
				S235F60	47.6	45.3	2.2	5
				Alu	37.1	35.4	1.7	5
				1.4401	36.8	35.8	1.0	5
B	36.1	30.8	5.3	S235	39.3	38.9	0.4	5
				S235gvz	37.6	34.2	3.4	5
				S235F60	47.6	45.3	2.2	5
				Alu	37.1	35.4	1.7	5
				1.4401	36.8	35.8	1.0	5

Fig. 3: Load capacity of metal bonding with different adhesives on different metals

The results show that adhesives show very different adhesive behaviour (Fig. 3). Stainless steel and aluminium have the lowest surface energies of the materials used here. They are approximately equal to the surface tensions of the adhesives U and B and achieve the highest loads in combination.

The assessment of adhesion via theoretical approaches provides partly useful results that are in line with practice. Many test results show a tendency of a correlation between wettability and adhesion. However, there are also results that do not show a relation, which indicates an insufficient theory. Therefore, it is currently not possible to calculate the strength of the boundary layer bond of a bond from the interfacial energy values [3, 5].

REFERENCES

[1]   https://de.wikipedia.org/wiki/Benetzung, 12/07/2018

[2]   HIRSCH, G.: *Bestimmung der Oberflächenspannung von Festkörpern aus Randwinkelmessungen und ihre Bedeutung bei Benetzungsproblemen.* Verlag Chemie GmbH, Weinheim, 1968

[3] HABENICHT, G.: *Kleben. Grundlagen, Technologien, Anwendungen. 6. Auflage.* Springer Verlag, Berlin, Heidelberg, 2009

[4] GLEICH, H.: *Zusammenhang zwischen Oberflächenenergie und Adhäsionsvermögen von Polymerwerkstoffen.* Dissertation, Duisburg, 2004

[5] RASCHE, M.: *Handbuch Klebetechnik.* Carl Hanser Verlag, München, Wien, 2012

[6] GOLDSCHMIDT, S.: *BASF Handbuch Lackiertechnik.* Vincentz Network, Münster, 2014

[7] MOLLET, H., GRUBENMANN, A.: *Formulierungstechnik.* Wiley-VCH GmbH, Weinheim, 1968