1

Adhesion: Definition and Nomenclature

1.1 Introduction

To the layperson, adhesion is a simple matter of how well two different materials stick together, and adhesion measurements provide some indication of the force required to separate them. This chapter will steer the reader to a more scientific definition of adhesion that can be useful for a variety of purposes. Also included are comments on nomenclature and usage and a short review of the history of adhesion.

1.2 Adhesives—a Brief Historical Viewpoint

The perception of stickiness pervades the human race's most conventional practices. Resin exuding from a pine branch (Figure 1.1) and the sap from a dandelion (*Taraxacum officinale*) stem are just two of a plethora of natural examples that show with certainty that human beings have continuously been aware of the presence of adhesion (Pascoe, 2005). It is undeniable that for ages, hominids have made use of viscous liquids that set to semi-solids. Throughout the Paleolithic period, humans grouped together in small societies, for instance bands (i.e., consisting of no more than 100 individuals) (Kottak, 2010), and survived by gathering plants, fishing, or hunting wild animals (McClellan and Dorn, 2006). The Paleolithic period is distinguished by the use of knapped stone tools although at that time, humans used wood and bone tools as well (Waldorf, 1994). In the Upper Paleolithic (40,000 to 10,000 years ago), bone and stone points were glued with resin to wooden shafts to create spears (Pascoe, 2005). Researchers in South Africa discovered a primary indication of human-made arrows: they unearthed 64,000-year-old "stone points," which they suggested might be arrowheads. Closer examination of the antique weapons exposed remnants of blood and bone that provided evidence of their use. The arrowheads also carried traces of glue—plant-based resin that might have been used to fasten them onto a wooden shaft. The presence of glue implied that people were able to produce composite tools in which different elements produced from

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Figure 1.1 Illustration of needles, cones, and seeds of Scots pine (*Pinus sylvestris*). Original book source: Prof. Dr Otto Wilhelm Thomé *Flora von Deutschland, Österreich und der Schweiz* 1885, Gera, Germany. Permission granted to use under GFDL by Kurt Stueber. Modifications made by Floranet (https://en.wikipedia.org/wiki/Pine#/media/File:Illustration_Pinus_sylvestris0_new.jpg).

dissimilar materials are glued together to make a single artefact (BBC News, 2010). Colored pigments were found glued to the walls of Chauvet Cave (Figure 1.2) in Vallon-Pont-d'Arc in the Ardèche, France, to produce the earliest recognized cave paintings, dated to about 40,000 years ago. In the first dynasty of ancient Egypt (c. 3000 BC), adhesives produced from natural materials were used to attach inlays to furniture (Pascoe, 2005). Inlays involve a variety of sculpting and decorative techniques to insert pieces of contrasting, frequently colored materials into depressions in a base object to form an ornament or pictures that are normally flush with the matrix (Fleming and Honour, 1977).

Ancient adhesives were composed of organic products, with carbohydrates, proteins, and hydrocarbons as the main ingredients. These were often transformed

Figure 1.2 Lion painting in Chauvet Cave. This is a replica of the painting from the Anthropos museum in Brno, Czech Republic. The absence of a mane sometimes leads to these paintings being described as portraits of lionesses. Author: HTO (source: https://en.wikipedia.org/wiki/Chauvet_Cave#/media/File:Lions_painting,_Chauvet_Cave_(museum_replica).jpg).

by aging, enzymatic action, hydrolysis, and oxidation, or processed by heat treatment (Pascoe, 2005). Once they have wetted the surfaces to be joined, adhesives must be converted to a solid of adequate strength over a suitable period. A number of mechanisms were used to transform liquids into solids, including coagulation of dispersions, ionic crosslinking, freezing, and solvent or carrier evaporation (Pascoe, 2005). Adhesion to wood, textiles, or skin products is frequently determined by hydrogen-bonding forces. Natural polymers are used not only in adhesives but also in many other applications, such as inks, paint binders, sealants, and varnishes. Due to the natural variability in the chemical composition of the ingredients, inconsistent performance of the mixtures may be expected; the adhesives are then better classified predominantly in relation to their use and not exclusively for their chemical, geographical, or historical attributes (Pascoe, 2005).

Waxes, tars, and bitumen (a sticky, black, and highly viscous liquid or semi-solid form of petroleum) (Figure 1.3) can be used upon melting as hot-melt adhesives (Sörensen and Wichert, 2009). Gum exudates, shellac (a resin secreted by the female lac bug on trees in the forests of India and Thailand) (Woods, 1994) and fossilized resins can have similar uses (Pascoe, 2005). Since handling of hot-melt adhesives is not easy, their uses are restricted. Although wax binders for pigments were used in durable paintings, painters favored more controllable ingredients (Pascoe, 2005). Numerous adhesives are based upon non-aqueous solvents, and their use requires technical expertise and distillation equipment to produce those solvents. Although alcohols and hydrocarbon solvents (i.e. turpentine) can be powerful solvents, water remains the most attractive one for sugars, gums, and proteins of various origins. From time to time, these

Figure 1.3 Naturally formed bitumen collected from the Dead Sea shore. Author: Daniel Tsvi (source: https://commons.wikimedia.org/wiki/File:Bitumen.jpg).

materials go through heat-processing, that is, prolonged boiling, which hydrolyzes and breaks up the large insoluble polymer molecules into smaller soluble entities (Pascoe, 2005). Consequently, gelatin glues are manufactured from bone collagen (the main structural protein in the extracellular spaces of various connective tissues in animals, skin, fins, and other fish parts) (Di Lullo et al., 2002). The resultant glues are very viscous and are therefore less effective at penetrating into substrate pores (gaps). Appropriate surfaces are not only porous but enable bonding to –OH or –NH groups in the glues (Pascoe, 2005).

Aqueous-dispersion adhesives are characterized by comparatively low viscosities and a fairly high solids content. As a result, they are beneficial for gap filling. Emulsion and starch pastes (often produced from cheap starch cereals) are customarily used in the mounting of Japanese scroll paintings. However, starch-paste joints are subject to aqueous and biochemical breakdown. Comparable to water-soluble adhesives, they can only be used on hydrophilic surfaces such as paper, skin, and wood (Pascoe, 2005). In nature, many plants and trees produce latex, which has low viscosity and a high solids content. Latex is a sticky, milky colloid that is drawn off by making incisions in the bark and accumulating the fluid in vessels in a procedure termed "tapping." Such latices can be coagulated to make several types of rubber objects, but they can be used as adhesives as well (Paterson-Jones et al., 1990; Pascoe, 2005). Compared to vulcanized rubber (vulcanization is a chemical process that converts natural rubber into a more durable material via the addition of sulfur or other equivalent curative or accelerator), uncured rubber has relatively few uses—in cements and adhesives, for insulation and in friction tapes, and for crepe rubber, which is used to insulate blankets and footwear (https://en.wikipedia.org/wiki/Vulcanization). A significant tonnage of rubber is used as adhesives in many manufacturing industries and products, but predominantly the paper and carpet industries.

Studies of adhesives on ancient objects are complicated by deterioration of the adhesives, which commonly causes superficial color alterations and embrittlement. In numerous maintenance operations, damaged adhesives have to be removed, often by dissolution, and replaced (Pascoe, 2005). Ancient adhesives are frequently insoluble and intractable, although there are some resourceful treatments to soften and effectively remove materials such as shellac with polar solvents, for instance pyridine (Figure 1.4), or aged starch, *N*-methylpyrrolidone (Figure 1.5), which has saved many an ancient master's drawings by separating them from detrimental acidic backing boards. Additional methods for softening animal protein glues on papyrus call for the use of proteolytic enzymes, and with some other pastes, amylase preparations are effective (Pascoe, 2005). Brittleness may actually be beneficial since woodworking joints may be fragmented by sharp impact and the remains are more easily scraped off. Obstinate adhesive residues may be similarly removed through the use of energetic argon-oxygen plasma cleaning, which gradually oxidizes organic materials into volatile gases. The plasma is produced by means of high-frequency voltage (typically kHz to > MHz) to ionize the low-pressure gas (typically around 1/1000th atmospheric pressure) (Kolluri, 2003; Pascoe, 2005). Primeval craftwork involved the selection of techniques and materials that had to be of animal, botanical, mineral, or piscine origin. The diversity of those materials is extraordinarily extensive. Considerable strength could not be achieved in most applications, particularly when large areas were involved. Bonding materials for substantial structural strength were not practical prior to the invention of synthetic adhesives along with more trustworthy methods for surface preparation before gluing (Pascoe, 2005). In conclusion, some adhesives were noticeably beneficial since they were naturally tacky, for instance, tree gums and rubbers. Use of other adhesives depended on the skilled use of fire, including carefully controlled melting and cooking. Sealing-wax mixtures, for example, beeswax and rosin—mainly abietic acid (Figure 1.6)—necessitated cautious control, especially while dispensing

Figure 1.4 Structural formula of the pyridine molecule, a simple aromatic heterocyclic compound. Author: Jynto (source: https://commons.wikimedia.org/wiki/File:Pyridine-2D-full.svg).

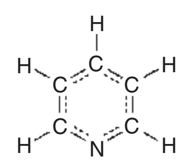


Figure 1.5 *N*-methylpyrrolidone structural formula. Author: Jü (source: https://commons.wikimedia.org/wiki/File:N-Methylpyrrolidone_Structural_Formulae.png).

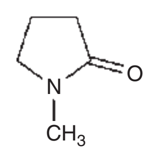
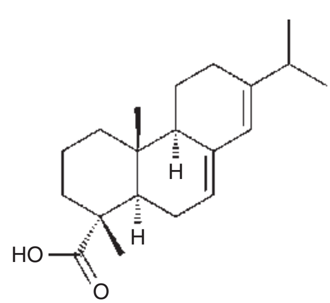


Figure 1.6 Structure of abietic acid, a component of rosin. (Source: https://commons.wikimedia.org/wiki/File:Abietic_acid.svg).



and stirring. Rosin is a solid form of resin obtained from pines and some other plants, frequently conifers, by heating fresh liquid resin to vaporization of the volatile liquid terpene constituents (Palkin and Smith, 1938). As already noted, such abilities and processes were very difficult to control. Craft reticence would have hindered the transference of these skills to other professionals; in any event, assessment and standardization would not have occurred until industrial development forced providers to preserve quality standards (Pascoe, 2005).

1.3 Nomenclature and Definitions of Adhesion Terms

1.3.1 Adhere

The word "adhere" comes from the Middle French *adhérer* or directly from the Latin *adhaerare*, meaning "to stick to" (Collins English Dictionary, 2009; Dictionary.com). Adhere means to cause two surfaces to be held together by adhesion (Hartshorn, 1986).

1.3.2 Adherend

In chemistry, an adherend is any substance that is bonded to another by an adhesive (Dictionary.com). The adherend is a body that is held to another body by an adhesive (Hartshorn, 1986).

1.3.3 Adhesion

Adhesion is the state in which two surfaces are held together by interfacial forces, which may consist of valence forces, interlocking action, or both (Hartshorn, 1986).

1.3.4 Adhesion Ability in Insects and the Gecko

An arthropod is an invertebrate animal of the large phylum Arthropoda, for example, insects, spiders, or crustaceans (http://www.dictionary.com/browse/arthropod). The arthropod (from the Greek *arthro*, joint + *podos*, foot) has an external skeleton, a segmented body, and jointed appendages (i.e., an external body part or natural prolongation that protrudes from an organism's body). Arthropods make use of smooth adhesive pads along with hairy pads to ascend a steep object or make any such movements that result in progression from one place to another along non-horizontal surfaces (https://en.wikipedia.org/wiki/Insect_adhesion) (Barnes and Jon, 2011; Jan-Henning and Federle, 2011). In insects, both smooth adhesive pads and hairy pads make use of fluid discharges and are considered "wet" (Bullock et al., 2008). Van der Waals forces might help explain the mechanisms of dry adhesion that can be observed in organisms other than insects (Von Byern and Grunwald, 2010). Although the compositions of such liquid secretions are not fully known, they afford both capillary and viscous adhesion and seem to exist in all insect adhesive pads (Zhou et al., 2014). Furthermore, mutually hairy and smooth forms of adhesion have evolved distinctly many times in insects (Gorb et al., 2007), and tree frogs as well as some mammals, such as the arboreal possum and bats, similarly use smooth adhesive

Figure 1.7 Close-up of the underside of a gecko's foot as it walks on a glass wall. Courtesy of Bjørn Christian Tørrissen (source: http://bjornfree.com/galleries.html).

pads. Appropriate adhesion allows these organisms to climb on almost any substance (Barnes and Jon, 2011).

Geckos are lizards belonging to the infraorder Gekkota, found in warm climates throughout the world (https://en.wikipedia.org/wiki/Gecko). Geckos have astonishing adhesive capabilities related to the millions of dry, adhesive setae (i.e., hair-like structures that derive from interactions between the oberhautchen and clear layers of the epidermis) on their toes (Alibardi, 1997; Kellar and Peattie, 2002). Each epidermis-derived, keratinous seta terminates in hundreds of 200-nm spatular tips, permitting intimate contact with rough and smooth surfaces alike (Figure 1.7). For a single seta, a small normal preload combined with a 5-μm displacement yielded a very large adhesive force of 200 micronewtons (μN), 10 times that predicted by whole-animal measurements. Upon maximal attachment, the 6.5 million setae of a single tokay gecko (a nocturnal arboreal gecko, ranging from northeast India, Bhutan, Nepal, Bangladesh, throughout Southeast Asia and the Philippines to Indonesia and western New Guinea) could generate 130 kg force. Increasing the angle between the setal shaft and the substrate to 30° causes detachment (Kellar and Peattie, 2002).

1.3.5 Adhesive

In physics, "adhesive" is the molecular force of attraction in the area of contact between unlike bodies that holds them together (based on the Random House Dictionary, Random House, Inc., 2015). An adhesive is any substance applied to the surfaces of materials that binds them together and resists separation (Kinloch, 1987). The term "adhesive" might be used interchangeably with glue, cement, mucilage, or paste (Hartshorn, 1986). Adjectives may be used in combination with the word "adhesive" to designate properties based on the substance's physical or chemical form, the type of materials joined, or conditions under which it is applied (Kinloch, 1987). Adhesives are typically systematized by the method of adhesion. These are then organized into reactive and non-reactive adhesives. Alternatively, they can be systematized by the origin of the raw stock, that is, whether it is of natural or synthetic origin, or by their initial physical phase (Kinloch, 1987).

1.3.6 Adhesive Assembly

An adhesive can be used to bond parts together. The reader is referred to Chapter 8 and the discussion about multilayered foods. Biocompatible, biodegradable, and/or non-toxic emulsion-based formulations have great potential for applications in foods. The combination of particular characteristics, such as emulsifying, antiadhesive (eliminating the ability to construct assemblies), and antimicrobial (presented by biosurfactants) suggests potential application as a multipurpose ingredient or additive (Kralova and Sjoblom, 2009).

1.3.7 Adhesive Bonding

Adhesives are being utilized more and more in the production of an extensive range of engineering components because of the considerable advantages provided by adhesive bonding in comparison to more customary joining techniques, such as riveting and welding (Pascoe, 2005). Adhesive bonding offers an efficient means of joining components, with many advantages over traditional fastening methods; nevertheless, its Achilles' heel is a weakening in strength as a consequence of weathering. Adhesive bonding (also denoted as gluing or glue bonding) defines a wafer bonding technique with spreading over an intermediate layer to join substrates of different materials. These manufactured connections can be soluble or insoluble. The commercially available adhesive can be organic or inorganic and is deposited on one or both substrate surfaces (Gessner et al., 2004). Suitable surface handling is crucial in preparing surfaces for adhesive bonding that will guarantee decent early strength along with long-term performance in service (Anon, 1990; Pascoe, 2005). The removal of surface contamination with consequent enhancement of surface energy and lowering of contact angle is a major objective of pretreatment prior to adhesive bonding, painting, or printing (Adamson and Gast, 1997). Anodic treatments find application in structural adhesive bonding where durability under hostile operational conditions is of paramount importance (Krieger, 1990; Critchlow and Brewis, 1996; Davis and Venables, 2002; Bjorgum et al., 2003).

1.3.8 Bacterial Adhesion

Adhesion is a crucial step in bacterial pathogenesis or infection, essential for colonizing a new host (Coutte et al., 2003). Bacteria are typically found attached or living adjacent to host surfaces (Klemm and Schembri, 2000). Bacterial adhesion has been interpreted in terms of hydrophobicity or surface free energy (Absolom et al., 1983; Busscher et al., 1984; van Loosdrecht et al., 1987b). Bacterial adhesion is also influenced by electrical charges of the bacteria and solid surfaces (Marshall et al., 1971; Larsson and Glantz, 1981; Hermansson et al., 1982; Gordon and Millero, 1984). Most natural solid surfaces, as well as bacteria, are negatively charged (Loder and Liss, 1985). The relationships between physicochemical surface parameters and adhesion of bacterial cells to negatively charged surfaces have been studied. Electrokinetic potential and cell-surface hydrophobicity were determined and both parameters were found to affect cell adhesion (van Loosdrecht et al., 1987b). The effect of electrokinetic potential increased with decreasing hydrophobicity. Cell-surface characteristics determining adhesion are influenced by growth conditions. At high growth rates, bacterial cells tend to be more hydrophobic. This can be of ecological importance for monitoring the spread of bacteria in the environment (van Loosdrecht et al., 1987a). Throughout its life cycle, a bacterium is subjected to recurrent shear forces. Bacterial adhesins serve as anchors, allowing the bacteria to overcome these environmental shear forces, and consequently survive in their selected niche (Klemm and Schembri, 2000). Bacterial adhesins perform like specific surface-recognition molecules, allowing the targeting of a particular bacterium to a specific surface, for example, root tissue in plants, lacrimal duct tissues in mammals, or even tooth enamel (Klemm and Schembri, 2000).

1.3.9 Cell-Adhesion Molecules

Cell-adhesion molecules (CAMs) help cells stick to each other and to their surroundings. They are proteins located on the cell surface that are involved in binding with other cells or with the extracellular matrix in the process of cell adhesion (https://en.wikipedia.org/wiki/Cell_adhesion_molecule). Most CAMs belong to four protein families (Brackenbury et al., 1981): immunoglobulin superfamily, the integrins (Brown and Yamada, 1995), the cadherins (Buxton and Magee, 1992), and the selectins (Ley, 2003).

1.3.10 Contact Adhesive

An adhesive that is apparently dry to the touch and will adhere to itself instantaneously upon contact; also termed contact bond adhesive or dry bond adhesive (Hartshorn, 1986).

1.3.11 Contact Mechanics

Contact mechanics is the study of the deformation of solids that touch each other at one or more points (Johnson, 1985; Popov, 2010).

1.3.12 Lateral Adhesion

Lateral adhesion is the adhesion associated with sliding one object across a substrate. It can be measured with a centrifugal adhesion balance, which uses a combination of centrifugal and gravitational forces to decouple the normal and lateral forces in the problem (https://en.wikipedia.org/wiki/Adhesion). This is a novel instrument that enables first-time measurements of the lateral adhesion forces at a solid–liquid interface, decoupled from normal forces (Tadmor et al., 2009).

1.3.13 Mechanisms of Adhesion

There is no one outstanding or unified theory of adhesion. Proven mechanisms are specific to particular material setups. Five mechanisms of adhesion have been suggested to clarify why one material adheres to another: (i) mechanical adhesion (i.e., adhesion between surfaces in which the adhesive holds the parts together by interlocking action) (Hartshorn, 1986); (ii) chemical adhesion (Kendall, 1994); (iii) dispersive adhesion (Kendall, 1994; Huang et al., 2005); (iv) electrostatic adhesion; and (v) diffusive adhesion (Maeda et al., 2002). These mechanisms are detailed for foods in this book and the reader is referred to Chapter 2.

1.3.14 Mucoadhesion

Mucoadhesion describes the attractive forces between a biological material and mucus or a mucous membrane (Smart, 2005). Mucoadhesion comprises numerous types of bonding mechanisms. The main theoretical types include wetting, adsorption, diffusion, electrostatic, and fracture theory (Amit et al., 2010; Shaikh et al., 2011). Those theories are discussed in detail in the following chapters.

1.3.15 Pressure-Sensitive Adhesives (PSAs)

A PSA is a viscoelastic material that, in solvent-free form, remains permanently tacky. Such material will adhere instantaneously to most solid surfaces with the application of very slight pressure (Hartshorn, 1986). Methods to test probe tack of PSAs (Figure 1.8) and the physical properties of these entities have been studied by many scientists (Ben-Zion and Nussinovitch, 2008; Shcherbina et al., 2010). Future trends and research directions for PSAs, from the point of view of their end-use properties, are moving toward heterogeneous polymer structures and the incorporation of additional functions, such as thermal or electrical conductivity or controlled drug release, as in nicotine patches, into a PSA matrix without altering its self-adhesive properties (Creton, 2003, Nussinovitch, 2009). It is also evident that the nano revolution, as has been discussed for edible coatings, will also be part of adhesives' future. Evidence for this can be found in a study that included nano-organoclays in PSAs. During drug release with these adhesives, the initial burst was reduced and could be controlled. Moreover, by optimizing the level of organo-silicate additive in the polymer matrix, superior control over drug-release kinetics and simultaneous improvements in adhesive properties could be attained for a transdermal PSA formulation (Shaikh et al., 2007; Nussinovitch, 2009).

1.3.16 Strength of Adhesion

The strength of the adhesion between two materials depends on which of the adhesion mechanisms (i.e., mechanical, chemical, dispersive, electrostatic, diffusive) is acting between the two materials, and the surface area over which the two materials are in contact (Hartshorn, 1986).

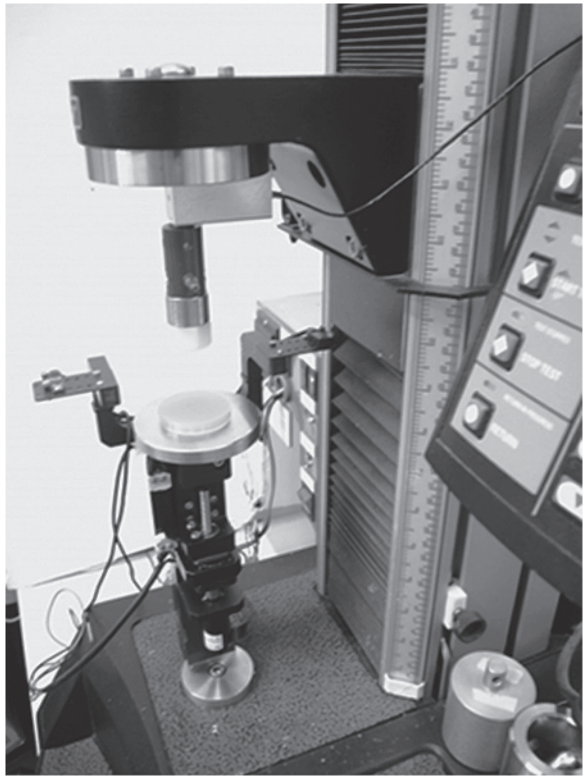


Figure 1.8 Custom-made apparatus attached to a universal testing machine to measure the probe tack of pressure-sensitive adhesives.

1.3.17 Wettability

Wetting is a fluid's ability to preserve contact with a solid surface, subsequent to intermolecular interactions when the two are brought together. The degree of wetting (wettability) is determined by a balance between adhesive and cohesive forces. Dewetting defines the rupture of a thin liquid film on the substrate (either a fluid itself, or a solid) and the formation of droplets (https://en.wikipedia.org/wiki/Dewetting).

1.4 Concluding Remarks

An adhesive is basically defined by its function, which is to hold two surfaces together. To fulfill this function, the properties of an adhesive must include easy positioning at the interface, rapid and complete bond formation and subsequent hardening, and a bond strength that is adapted to the specific application (structural, permanent, removable, rigid, or soft) (Creton and Papon, 2003). A variety of solutions exist in practice, and their application requires an understanding of both polymer chemistry and materials science (Creton and Papon, 2003). There is a close link between mechanics, chemistry, and physics when it comes to adhesion. Nature offers a rich trove of solutions for numerous surface-related problems in materials science. However, these can only be mimicked, leading to a thorough consideration of functional principles (Gorb, 2006). Examples from biology highlight the significance of mechanics, but then again the simulated solutions are not achievable without a combination of clever mechanical design and well-adapted material solutions (Gorb, 2006). Engineered adhesive nanostructures inspired by geckos (the adhesive on gecko toes differs dramatically from that of conventional adhesives) may become the glue of the future, but it is too early to tell, and therefore difficult to estimate whether hydrocolloids will take part in this development (Autumn, 2007). The challenge for the study of adhesives is to move away from chemistry and suggest systems that can provide a solution for explicit requests. These different materials would be made up of distinct phases with an internal organization that can be adapted to a specific substrate (Aymonier and Papon, 2003). Moreover, some additional areas of expansion can be imagined, such as preparation of new adhesive systems using innovative polymer architectures leading to the desired organization (Aymonier and Papon, 2003).

References

Absolom, D.R., Lamberti, F.V., Policova, Z., Zingg, W., van Oss, C.J., and Neumann, A.W. (1983) Surface thermodynamics of bacterial adhesion. *Appl. Environ. Microbiol.*, 46, 90–97.

Adamson, A.W. and Gast, A.P. (1997) *Physical Chemistry of Surfaces*, 6th edn. Chichester, UK: John Wiley & Sons, Ltd.

Alibardi, L. (1997) Ultrastructural and autoradiographic analysis of setae development in the embryonic pad lamellae of the lizard Anolis lineatopus. *Annales des Sciences Naturelles Zoologie et Biologie Animale* 18, 51–61.

Amit, A., Charma, S., and Khad, M. (2010) Theories and factor affecting mucoadhesive drug delivery systems: a review. *Journal of Advanced Pharmaceutical Technology and Research* 1, 381–387.

Anon (1990) *Adhesive Bonding Handbook for Advanced Structural Materials*. Noordwjik, The Netherlands: European Space Research and Technology Centre, European Space Agency.

Autumn, K. (2007) Gecko adhesion: structure, function, and applications. *Materials Research Society Bulletin* 32, 473–478.

Aymonier, A. and Papon, E. (2003) Designing soft reactive adhesives by controlling polymer chemistry. *Materials Research Society Bulletin* 28, 424–427.

Barnes, W. and Jon, P. (2011) Functional morphology and design constraints of smooth adhesive pads. *Materials Research Society Bulletin* 32, 479–485.

BBC News (2010) Oldest evidence of arrows found. Archived from the original on August 26, 2010. Retrieved January 11, 2015 at: http://www.bbc.com/news/science-environment-11086110.

Ben-Zion, O. and Nussinovitch, A. (2008) A modified apparatus for testing the probe tack of pressure-sensitive adhesive materials. *Journal of Adhesion Science and Technology* 22, 205–216.

Bjorgum, A., Lapique, F., Walmsley, J., and Redford, K. (2003) Anodizing as pre-treatment for structural bonding. *International Journal of Adhesion and Adhesives* 23, 401–412.

Brackenbury, R., Rutishauser, U., and Edelman, G.M. (1981) Distinct calcium-independent and calcium-dependent adhesion systems of chicken embryo cells. *Proceedings of the National Academy of Sciences of the USA* 78, 387–391.

Brown, K. and Yamada, K. (1995) The role of integrins during vertebrate development. *Developmental Biology* 6, 69–77.

Bullock, J.M., Drechsler, P., and Federle, W. (2008) Comparison of smooth and hairy attachment pads in insects: friction, adhesion and mechanisms for direction-dependence. *Journal of Experimental Biology* 211, 3333–3343.

Busscher, H.J., Weerkamp, A.H., van der Mei, H.C., van Pelt, A.W.J., de Jong, H.P., and Arends, J. (1984) Measurement of the surface free energy of bacterial cell surfaces and its relevance for adhesion. *Applied Environmental Microbiology* 48, 980–983.

Buxton, R.S. and Magee, A.I. (1992) Structure and interactions of desmosomal and other cadherins. *Seminars in Cell Biology* 3, 157–167.

Collins English Dictionary (2009) Complete & Unabridged 10th Edition. Harper Collins Publishers.

Coutte, L., Alonso, S., Reveneau, N., et al. (2003) Role of adhesin release for mucosal colonization by a bacterial pathogen. *Journal of Experimental Medicine* 197, 735–742.

Creton, C. (2003) Pressure-sensitive adhesives: an introductory course. *Materials Research Society Bulletin* 28, 434–439.

Creton, C. and Papon, E. (2003) Materials science of adhesives: how to bond things together. *Materials Research Society Bulletin* 28, 419–421.

Critchlow, G.W. and Brewis, D.M. (1996) Review of surface pretreatments for aluminium alloys. *International Journal of Adhesion and Adhesives* 16, 255–275.

Davis, G.D. and Venables, J.D. (2002) Surface treatment of metal adherends. In: *Adhesion Science and Engineering – 2, Surfaces, Chemistry and Applications* (eds M.K. Chaudhury and A.V. Pocius). Amsterdam: Elsevier, pp. 947–1008.

Dictionary.com. Website: http://dictionary.reference.com/browse/(accessed June 20, 2016).

Di Lullo, G.A., Sweeney, S.M., Körkkö, J., Ala-Kokko, L., and San Antonio, J.D. (2002) Mapping the ligand-binding sites and disease-associated mutations on the most abundant protein in the human, Type I Collagen. *Journal of Biological Chemistry* 277, 4223–4231.

Fleming, J. and Honour, H. (1977) *The Penguin Dictionary of the Decorative Arts.* New York: Viking Books.

Gessner, T., Otto, T., Wiemer, M., and Frömel, J. (2004) Wafer bonding in micro mechanics and microelectronics – an overview. In: *The World of Electronic Packaging and System Integration* (eds B. Michel and R. Aschenbrenner). Dresden: DDP Goldenbogen, pp. 307–313.

Gorb, S.N. (2006) Functional surfaces in biology: mechanisms and applications. In: *Biomimetics: Biologically Inspired Technologies* (ed. Y. Bar-Cohen). Boca Raton, FL: CRC Press, pp. 381–397.

Gorb, S.N., Sinha, M., Peressadko, A., Daltorio, K.A., and Quinn, R.D. (2007) Insects did it first: a micropatterned adhesive tape for robotic applications. *Bioinspiration & Biomimetics* 2, S117–S125.

Gordon, A.S. and Millero, F.J. (1984) Electrolyte effects on attachment of an estuarine bacterium. *Applied Environmental Microbiology* 47, 495–499.

Hartshorn, S.R. (1986) *Structural Adhesives, Chemistry and Technology*. New York and London: Plenum Press.

Hermansson, M., Kjelleberg, S., Korhonen, T.K., and Stenstrom, T.-A. (1982) Hydrophobic and electrostatic characterization of surface structures of bacteria and its relationship to adhesion to an air-water interface. *Archives of Microbiology* 131, 308–312.

Huang, Y.Y., Zhou, W., Hsia, K.J., et al. (2005) Stamp collapse in soft lithography. *Langmuir* 21, 8058–8068.

Jan-Henning, D. and Federle, W. (2011) Fluid-based adhesion in insects—principles and challenges. *Soft Matter* 7, 11047–11053.

Johnson, K.L. (1985) *Contact Mechanics*. Cambridge, UK: Cambridge University Press.

Kellar A.K. and Peattie, A.M. (2002) Mechanisms of adhesion in geckos. *Integrative and Comparative Biology* 42, 1081–1090.

Kendall, K. (1994) Adhesion: molecules and mechanics. *Science* 263, 1720–1725.

Kinloch, A.J. (1987) *Adhesion and Adhesives: Science and Technology* (reprinted edn). London: Chapman & Hall.

Klemm, P. and Schembri, M.A. (2000) Bacterial adhesins: function and structure. *International Journal of Medical Microbiology* 290, 27–35.

Kolluri, O.S. (2003) Application of plasma technology for improved adhesion of materials. In: *Handbook of Adhesive Technology, Revised and Expanded*, 2nd edn (eds A. Pizzi and K.L. Mittal). Boca Raton, FL: CRC Press, pp. 193–205.

Kottak, C.P. (2010) *Cultural Anthropology: Appreciating Cultural Diversity*, 14th edn. New York: McGraw-Hill.

Kralova, I. and Sjoblom, J. (2009) Surfactants used in food industry: a review. *Journal of Dispersion Science and Technology* 30, 1363–1383.

Krieger, R.B. (1990) Adhesive bonding design and analysis. In: *ASM Engineered Materials Handbook. Vol. 3: Adhesives and Sealants* (ed. M.M. Gauthier). Materials Park, OH: ASM International, p. 459.

Larsson, K. and Glantz, P.O. (1981) Microbial adhesion to surfaces with different surface charges. *Acta Odontologica Scandinavica* 39, 79–82.

Ley, K. (2003) The role of selectins in inflammation and disease. *Trends in Molecular Medicine* 9, 263–268.

Loder, T.C. and Liss, P.S. (1985) Control by organic coatings of the surface charge of estuarine suspended particles. *Limnology and Oceanography* 30, 418–421.

Maeda, N., Chen, N., Tirrell, M., and Israelachvili, J.N. (2002) Adhesion and friction mechanisms of polymer-on-polymer surfaces. *Science* 297, 379–382.

Marshall, K.C., Stout, R., and Mitchell, R. (1971) Mechanisms of the initial events in the sorption of marine bacteria to surfaces. *Journal of General Microbiology* 68, 337–348.

McClellan, J.E. and Dorn, H. (2006) In: *Science and Technology in World History: An Introduction*. Baltimore, MD: Johns Hopkins University Press, pp. 6–12.

Nussinovitch, A. (2009) Hydrocolloids for coatings and adhesives. In: *Handbook of Hydrocolloids*, 2nd edn (eds G.O. Phillips and P.A. Williams). Boca Raton, FL: CRC Press; and Cambridge, UK: Woodhead Publishing Ltd, pp. 760–806.

Palkin, S. and Smith, W.C. (1938) A new non-crystallizing gum rosin. *Oil & Soap* 15, 120–122.

Pascoe, M.W. (2005) Adhesives – historical perspective. In: *Handbook of Adhesion*, 2nd edn (ed. D.E. Packham). Chichester, UK: John Wiley & Sons Ltd, pp. 28–32.

Paterson-Jones, J.C., Gilliland, M.G., and Van Staden, J. (1990) The biosynthesis of natural rubber. *Journal of Plant Physiology* 136, 257–263.

Popov, V.L. (2010) *Contact Mechanics and Friction. Physical Principles and Applications*. Berlin/Heidelberg: Springer-Verlag.

Shaikh, S., Birdi, A., Qutubuddin, S., Lakatosh, E., and Baskaran, H. (2007) Controlled release in transdermal pressure sensitive adhesives using organosilicate nanocomposites. *Annals of Biomedical Engineering* 35, 2130–2137.

Shaikh, R., Raj Singh, T.R., Garland, M.J., Woolfson, A.D., and Donnelly, R.F. (2011) Mucoadhesive drug delivery systems. *Journal of Pharmacy and Bioallied Sciences* 3, 89–100.

Shcherbina, Y., Roth, Z., and Nussinovitch, A. (2010) Physical properties of gum karaya-starch-essential oil patches. *AAPS PharmSciTech* 11, 1276–1286.

Smart, J.D. (2005) The basics and underlying mechanisms of mucoadhesion. *Advanced Drug Delivery Reviews* 57, 1556–1568.

Sörensen, A. and Wichert, B. (2009) Asphalt and bitumen. In: *Ullmann's Encyclopedia of Industrial Chemistry* (ed. B. Elvers). Weinheim, Germany: Wiley-VCH, pp. 273–294.

Tadmor, R., Bahadur, P., Leh, A., N'guessan, H.E., Jaini, R., and Dang, L. (2009) Measurement of lateral adhesion forces at the interface between a liquid drop and a substrate. *Physical Review Letters* 103, 266101–266104.

van Loosdrecht, M.C.M., Lyklema, J., Norde, W., Schraa, G., and Zehnder, A.J.B. (1987a) The role of bacterial cell wall hydrophobicity in adhesion. *Applied Environmental Microbiology* 53, 1893–1897.

van Loosdrecht, M.C.M., Lyklema, J., Norde, W., Schraa, G., and Zehnder, A.J.B. (1987b) Electrophoretic mobility and hydrophobicity as a measure to predict the initial steps of bacterial adhesion. *Applied Environmental Microbiology* 53, 1898–1901.

Von Byern, J. and Grunwald, I. (2010) *Biological Adhesive Systems: from Nature to Technical and Medical Application*, 1st edn. Vienna/New York: Springer.

Waldorf, D.C. (1994) *The Art of Flint Knapping*, 4th edn. Branson, MO: Mound Builder Books, p. 76.

Woods, C. (1994) The nature and treatment of wax and shellac seals. *Journal of the Society of Archivists* 15, 203–214.

Zhou, Y., Robinson, A., Steiner, U., and Federle, W. (2014). Insect adhesion on rough surfaces: analysis of adhesive contact of smooth and hairy pads on transparent microstructured substrates. *Journal of the Royal Society Interface* doi:10.1098/rsif.2014.0499.