Bioadhesives

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Abstract

Bioadhesion is a versatile tool used by many organisms for a variety of purposes. It has roles to play in construction, predation, defense, and attachment and covers different concepts based on biochemical and mechanical principles. The specific request on the bond combined with millions of years of evolution results in diverse inspirations for medical and technical applications. This requires knowledge of the adhesives themselves in terms of composition, structural design, and interaction with surfaces. This chapter gives an overview about natural adhesives and biological adhesives leading to bioinspired applications. The terminology used in this chapter is based on the adhesive's origin and usage and the underlying concept: while natural adhesives are composed of bio-based raw materials for artificial applications, biological adhesives are expressed by natural organisms for versatile purposes. The latter in particular can lead to bioinspired applications that are not restricted to adhesion, including concepts to avoid adhesion as in terms of antifouling. Both kinds of adhesive, i.e., natural and biological, are relevant for biocompatible adhesives. This characteristic is mandatory for applications as in cosmetics, food, or medicine. In view of their interaction with vital tissues and their medical eligibility, a brief digression into biomimetic adhesives is given.

54.1 Introduction

Bioadhesives are defined as natural polymers that act as adhesives. The compositions of bioadhesives are mostly complex and can contain proteins, carbohydrates, or lipids alone or complex mixtures with varying proportions. The first documented use of natural adhesives was 200,000 years ago by Neanderthals. They used tar from birch bark to join blades of rock with a shaft. Adhesives like wet lime, resins from trees, collagen, or semiliquid balsams were also used by the Egyptians, the Greeks, and the Romans for applications in marquetry, ceramics, and wood materials thousands of years ago. These adhesives had a natural origin in common. During the industrial revolution, the bioadhesives were replaced by synthetic ones. Nowadays the bioadhesive saga has reached a turning point, and new generations such as bioinspired and biomimetic adhesives are becoming more and more advanced (Mathias et al. 2016).

On the one hand, the increased focus on resource efficiency which is borne out from, among others, ecological needs is a major concern. Therefore natural adhesives are of particular interest. On the other hand, there is the challenging request of adhesion under harsh conditions like wet surfaces, which is excellently solved by marine organisms, many bacteria, and fungi. According to Aristotle, "If there is a better solution, nature has probably found it," and bioadhesives do indeed often provide inspiration and address needs like sustainability.

Adhesive materials and structures are used by many plants, animals, and microbes to attach themselves to inert substrates or to living tissue (Smith and Callow 2006; von Byern and Grunwald 2010; Smith 2016). Therefore, as for many technical applications, nature stands at parity for high-performance adhesion.

Among diverse purposes and complex raw materials, bioadhesives also serve solution approaches. The underlying principal mechanisms of adhesion are various. The octupus suction pad and the feet of geckos and flies, cases in which adhesion is achievd by physical means, are examples which show that biological adhesives do not necessarily have to involve complex biopolymers. Often the functional principles are worth investigating, and it is better to imitate these mechanisms than to attempt complete composition. Usually limited resources and high performance meet the technical requirements perfectly. There are three outstanding characteristics in connection with biological adhesion that are hardly reached by synthetic solutions: (i) bonding and debonding on demand, (ii) adhesion under wet conditions, and (iii) adherence to multiple substrates. The principle mechanisms of biological adhesion were classified into basically physical (interlocking, snap connection, staples, spreading device, suction, friction, capillary effects) and chemical (dry and wet adhesion). Sometimes different adhesion concepts are combined like interlocking, chemical interactions, as well as viscosity and capillarity forces (Schwotzer et al. 2012). Exemplary cases in particular for the chemical ones are reviewed in Sect. 3.

54.2 Natural Adhesives

Synthetic adhesives are required by industries in huge quantities for bonding nearly all kinds of substrates ranging from metal to human tissue. For many of these formulations, the environmental, health, and economic aspects are a matter of concern. There is an urgent need to substitute the majority of critical components deemed environmentally unsafe (Meyer-Rochow et al. 2015) such as phenol-formaldehyde or poly(vinyl acetate) (PVA) by biopolymers that are defined as high molecular mass compounds produced by living organism (Patachia and Croitoru 2016). Another objective is to avoid residual toxic chemicals such as volatile organic compounds (VOCs), epichlorohydrin, or methylene diphenyl diisocyanate (MDI). Beyond their composition, it is their end-of-life fate that has moved into focus (Erren et al. 2013). A global analysis of all mass-produced plastics ever manufactured revealed an estimated 8,300 million metric tons (Mt) of virgin plastics have been produced until 2017 of that less than 10% has been or can be recycled (Geyer et al. 2017). This scrutiny of the end-of-life management has also helped moving the focus to demands for recycling and degradation. The United States Environmental Protection Agency (US EPA) has already addressed these concerns, aiming to diminish the use of non-bioplastics in their pollution prevention program during the Obama administration (Gross and Kalra 2002). Despite the varying quality from batch to batch, adhesives originating from bioresources are commercially attractive, because of their numerous advantages like biodegradability, less toxicity, and natural biocompatibility. Today 15% of the adhesives are made out of renewable resources. The green content will increase in the next years by intensifying the use of second-generation biomass, which goes beyond the biofuel production used to synthesize biochemicals. There is a strong research and development focus to develop and commercialize the bioadhesive market. For adhesives and sealants, the market is being driven by a rising trend in various end user segments to use eco-friendly or green adhesives. The projected goal is to reach about 1.24 billion US dollars in 2017 (http://www.smithersapex.com/market-reports/green-adhesives-sealants-industrial-applications). The bio-based adhesive market size accounts for roughly 1–2% of the overall demand. Using novel feedstock such as vegetable oil polyamides, polyisoprenes, soybean polyols, or epoxies could lead to a paradigm shift and change the product matrix of natural adhesives significantly (http://www.adhesivesmag.com/articles/94808-auto-packaging-construction-lead-adhesives-and-sealants-market-growth).

Placed into eight "families," natural adhesives can be distinguished on the basis of their structure: nucleic acids, polyesters, polyisoprenoids, polyoxoesters, polyphenols, polysaccharides, polythioesters, and proteins (Kumar Patel et al. 2013). In the following sections, the most important species of natural adhesives are organized by source: starting with natural vegetable resins (rosin, terpene resins); followed by polyisoprenoids (natural rubber), natural polyesters (vegetable oil, shellac), carbohydrates (starch and dextrins, cellulose "derivatives," gums, and exopolysaccharides), and proteins (collagen, blood, and vegetable proteins); and closing with polyphenols (lignin, bitumen). For an excursus to natural cross-linkers (e.g., genipin from *Gardenia* spec.) or bio-based epoxy curing agents, the reader is directed to Sung et al. (1998) and Shibata (2013).

54.2.1 Natural Resins

Numerous plants use exudates for repair or healing issues in case of injuries. These natural resins are from the chemical point of view related to terpenes and etheric oils. They are amorphous and consist of complex mixtures (phenols, resin acids, resin alcohols, unsaturated resins, resin esters). Natural resins are considered as green raw material, but due to their structure, they are hardly biodegradable. Of particular importance are resin sources of pine trees. Their isoprenoid terpene rosin and terpene resins are valuable additives to provide tack and peel to the adhesive mixture. Their multiple properties offer versatile applications that range from the usage in the preparation of thermoplastics like polyesters (Karak 2016) to uses within the formulation, e.g., of pressure-sensitive adhesives. Their individual chemical structures make significant differences in terms of their compatibility with the formulation. For instance, terpene resin derivatives from pines are tolerated by styrene-butadiene rubber but not d-limonene. In sum, natural resins offer a high potential for adjusting adhesives within the bio-based toolbox.

Rosin

One of the oldest raw materials in the adhesion industry is rosin. It is used directly or converted to resin esters. Rosin is obtained from conifers and naturally synthesized as a defense compound. By distillation nonvolatile terpene components get separated from the fresh liquid resin. The semitransparent and colored solid has a piney odor and is brittle at ambient conditions. It consists out of abietic acid, an unsaturated monobasic acid, and additional organic acids. Three classes of rosins can be distinguished: (i) gum rosin (pine gum), the secreted oleoresin from wounds in the living pine tree; (ii) wood rosin, resinous extract from the pine wood stump that was left after harvesting of the tree in the ground for about 10 years to enrich the heartwood in resin; and (iii) tall oil rosin (TOR), a distillate of tall oil (liquid rosin) named after the Swedish word for pine oil “tallolja.” Tall oil is a by-product from Kraft pulping (sulfate process) when pulping coniferous trees. The yellow blackish liquid composed of fatty acids (palmitic, oleic, and linoleic) and rosin acids (mainly abietic) results in TOR with reduced rosin content by fractional distillation. If the rosin content is too high, the material is brittle. In this case additives like beeswax or powdered biochar improve the adhesive strength. In formulations with traditional linseed oil and sand, it is used as gap filler in constructions. Due to its improvement of gloss, hardening, or antifouling properties, rosin-modified alkyd resins or rosin derivatives are used in paints and surface coatings (Karak 2016).

Terpene Resins

Terpene resins are derivatives from turpentine (α-pinene, β-pinene, 3-carene) or can be obtained from citrus plants (d-limonene). Three major structural classes can be distinguished: styrenated terpene resins, terpene-phenol resins, and polyterpene resins. Terpene resins can be obtained from terpenes by cationic polymerization. The oldest reference for terpene resins goes back to 1789, when turpentine was treated with sulfuric acid. Terpene resins are used in a wide variety of formulations, e.g., coating compositions or adhesive tapes (Adhesives & Sealants, Industry News 2017: Materials and Chemicals Overview, http://www.adhesivesmag.com/articles/95737-materials-and-chemicals-overview). To impart the tack in solvent-based or hot melt adhesives, terpene resins from monoterpenes are used in additive manufacturing (NPCS Board of Consultants and Engineers 2017). Terpene resins are supplied in solution or in solid forms, the latter available in a wide range of molecular weights and softening points (Adhesives & Sealants, Industry News 2017: Materials and Chemicals Overview, http://www.adhesivesmag.com/articles/95737-materials-and-chemicals-overview).

54.2.2 Natural Rubber

Natural rubber adhesive is based on cis-1,4-isoprenoid units. It belongs to the earliest substances used to bind materials. Because of its capacity to become elastic when heated, it is one of the most popular adhesives on the market and is typically used in bonding organic and porous materials like leather, paper, fabrics, as well as other rubber products. The adhesive is based on natural rubber, an extract from latex, which is the milk of the rubber tree, *Hevea brasiliensis*. The milk is composed out of 60–75% water, 25–35% rubber, 1.5–2.5% resins, 1.5–2% proteins, and 0.5–1% minerals. Eight types of basic natural rubber are recognized: ribbed smoked sheets, pale crepes, estate brown crepes, compo crepes, thin brown crepes (remills), thick brown crepes (ambers), flat bark crepes, and pure smoked blanket crepes. The definition of these grades is described in the so-called Green Book (Cohen et al. 2008).

Natural rubber mixed with resin gives a sticky material, the adhesive. The unique chemical structure is responsible for its outstanding properties: high initial tack, excellent flexibility and tack retention. The cohesion is caused by the long entangled polymer chains of rubber and gives a highly elastic but brittle adhesive at low temperatures. By vulcanization, the addition of sulfur which acts as a cross-linker, the stability in terms of temperatures can be improved. The low strength due to the limited cohesion and adhesion at temperatures above 70 °C and the softening make it unsuitable for structural applications. Another disadvantage is the poor resistance to ultra violet radiation, ozone, organic solvents and oxidizing agents.

A well-known application is that for self-sealing envelopes. Also used in masking and cloth tapes, the compound found applications beyond those in packaging.

54.2.3 Natural Polyesters

Beeswax and vegetable oils belong to natural esters. While beeswax serves as appropriate softener within adhesive formulations but has no initial tack, the vegetable oils expose more suitable structures prerequisite to act as components in adhesives (Türünc et al. 2015). Vegetable oils are fatty acids or triglyceride esters from the seeds of plants (Karak 2016). The fatty acids, which are components of the triglycerides, can be saturated or unsaturated. Double bonds of unsaturated fatty acids are accessible for oxidation reactions, e.g., by cleavage or epoxidation. The modified oil gives access to dicarboxylic acids or epoxidized oils, respectively, which present appropriate reactive groups for formulations like pressure-sensitive adhesives (PSA) (Köckritz and Martin 2008; Li and Li 2014; Wu et al. 2015). Other than oxidation of double bonds, oleochemistry also uses hydrolysis to gain free fatty acids and glycerol or transesterification reaction to get fatty acid methyl esters (Türünc et al. 2015). Vegetable oil derivatives are preferably used for the polyester syntheses that have long-term durability and good adhesion. Advantages of triglycerides are their abilities to create three-dimensional networks and in case of ricinoleic acids from ricinolein (castor-oil-plant) an additional hydroxyl group, which serves as a natural polyol for polyurethanes.

Shellac

Lacca in tabulis, lac, or shellac, also wrongly referred to as gummi lacca, is the general term for the refined form of lac, a natural polyester resin secreted by tiny scale insects. These phytophagous insects (*Kerria lacca*, *Laccifer lacca*, *Laccifer chinensis*) insert their mouthpart into the barks of specific trees. The insects secrete a sticky lac after transforming the ingested sap into a polyester resin. Therefore it is the only natural resin of economic interest with an animal origin. Shellac is neither a biopolymer nor a monomer; it’s on a low level pre-polymerized. For refining issues to get shellac from the seed lac, three processes (bleaching, melting, and solvent extraction) are used. The resulting products vary in terms of characteristics like color and properties. Depending on the refining method, four types of shellac are distinguished: bleached shellac (regular bleached shellac), bleached dewaxed shellac (refined bleached shellac), wax-containing shellac (orange shellac), and dewaxed shellac (dewaxed orange shellac) (Sankaranarayanan 1989).

Orange shellac and bleached shellac have molecular weights of 1006 g/mol and 949 g/mol, respectively, and the empirical formula for the average shellac molecule is $C_{60}H_{90}O_{15}$. Even with this relatively low molecular weight, shellac has excellent film-forming properties, good adhesion to a variety of surfaces, high gloss and surface hardness, good insulation qualities (sealing out moisture), abrasion resistance, and excellent UV stability that prevents darkening, and moreover it is nontoxic. An alcoholic (ethanol or methanol) solution results in good durability. Its solubility in water in the presence of alkalis makes it attractive for cosmetic purposes like hair spray and drug delivery. It consists of a complex mixture of aliphatic and alicyclic acids (jalaric acid, schellolic acid, and aleuritic acid, also butolic and kerrolic acids). Beyond its usage as a colorant, brush-on, wood finish, and food glaze, shellac has historically been used as an adhesive for wooden layers on the hulls of boats (Penning 1996; Specht et al. 1998; Buch et al. 2009). Shellac is one of just a few known bio-based duroplastics (Türk 2014).

54.2.4 Carbohydrates

For many decades carbohydrates (monomeric, oligomeric, polymeric, and gum sugars) have been used as adhesives. Sugar and flour glue as well as corn starch glue are often used as homemade glues. The formulation is simple and the adhesive is versatile. These carbohydrates are chemically saccharides and appear in all organisms, namely, bacteria (xanthan gum and dextran), fungi (schizophyllan and scleroglucan), plants, and animals. Typically plants and animals often use the polymeric form (polysaccharides) as storage compounds (e.g., starch and glycogen), which can have adhesive properties. But polysaccharides are also used for cellular communication (glycosaminoglycans) or as structural biopolymers like chitin, alginates, chondroitin sulfate, or cellulose. Polysaccharides are eligible for adhesion because of the high density of polar functional groups and the high molecular weight leading to specific secondary structures (helical, sheet, or spiral conformation) due to noncovalent interactions. The degree of a carbohydrate's polymerization is highly dependent on origin, pretreatment, and measurement technology. The adhesion to substrates with high surface energy like wood or metals is favored by the polarity, while the cohesion benefits from conformational features. Both, adhesion and cohesion, benefit from the structural variability and can be enhanced by modifications of the functional groups (e.g., carboxylates or hydroxyl). Beyond the well-documented vegetable polysaccharide derivatives, chitosan with its origin in the exoskeleton (the most abundant polysaccharide after cellulose) of marine invertebrates and microbial exopolysaccharides show high potential for adhesives, especially for wood applications. In order to reduce the content of unwanted synthetically toxic components in commercial adhesive applications, one approach is to partly substitute them with polysaccharides. Hence, numerous adhesives made of polysaccharides as a co-component have been developed. They are known as intermediate (bio)adhesives (Kumar Patel et al. 2013; Karak 2016).

Carbohydrate-based epoxy resins also moved into a tighter focus as a potential alternative with improved physical properties and more efficient curing than petroleum-based epoxy resins. Based on recent studies, covetable epoxy resins may also be designed coming from furan or isosorbides. Furanyl building blocks prepared from pentose, hexose, or polysaccharides could replace petroleum-based phenyl building blocks in thermoset resins, while epoxidized isosorbide has already been shown to be a suitable and favored substitute of bisphenol A. Beyond the suitability of furan derivatives in epoxy-based resins, carbohydrate derivatives are under investigation as epoxy curing agents (Baroncini et al. 2016).

Cellulose Derivatives

Cellulosic adhesives are solvent-based thermoplastics. As polyhydroxyl alcohol with access to esterification and etherification reaction, esters and ether derivatives as well as polyblends of cellulose and cellulose graft copolymers provide a wide range of adhesive applications. Cellulose nitrate was the first inorganic ester derivative, and it is still one of the most important adhesives. It advanced to a famous “household” cement as it combines features like transparency, flexibility, and water indelibility with a wide range of solubility. Cellulose acetate butyrate is an ester that can be directly used in hot melt adhesives and is utilized in safety glass manufacture. Another ester, cellulose caprate, is used as hot and liquefied optical cement for the manufacture of compound lenses due to its good resistance against UV radiation and the possession of a refractive index near that of glass. Etherification of cellulose can open up the structure to enable solubility in water. The innate adhesive properties of cellulose ethers have been used as thickeners in adhesive formulations. They are of considerable industrial importance as their usage includes plywood adhesives, wallpaper and library pastes, latex adhesives, paper and textiles, and ceramic adhesives. Especially carboxymethlycellulose (CMC) is popular, because of its properties (nonstaining wallpaper adhesive, ease of slip/non-spoiling, high adhesive efficiency, and ease of makeup). Hence, CMC is appreciated in the ceramic industry due to its ability to act as a binder and to suspend materials during various stages of manufacture (Hon 1989).

For applications in adhesive technology, the polymeric degree and structure of cellulose derivatives, which has a direct impact on the solubility and swelling behavior, have to be considered in the preparation of suitable derivatives. In general the principle is valid: the higher the molecular weight, the higher its bond strength. For cellulosic adhesives, processing the adhesive becomes more difficult for increased molecular weights.

Cellulose is never met in pure form. It is a linear homopolysaccharide made up of glucose molecules. Due to its long linear structure, cellulose can achieve a degree of crystallinity of 60–80% depending on its age: the older the higher the crystallinity. Compared with starch and chitin, it has been revealed that even minor structural differences in the direction of the glycosidic bond (alpha or beta) decide if the conformation is linear or helical and therefore if it is soluble in aquatic media (Türk 2014). These characteristics are of major interest in terms of water resistance and biodegradation. In sum depending on the modification, cellulose may be available as soft as well as tough solvent-based formulations or as hot melts. It adheres very well to porous materials and exhibits substantial resistance to fouling and oil.

Starch and Dextrins

In the predynastic period, Egyptians treasured the practical use of starch when cementing it together with strips of papyrus. They boiled wheat flour with dilute vinegar to obtain an adhesive. Adhesives made from starch and dextrins are almost solely water based and used mainly in the paper and packaging industry. Especially the increasing sector of cardboard and corrugated board production suggests a rising demand. Also as bookbinder adhesive, it occupies a considerable niche market. Starch is a mixture of linear amylose and branched amylopectin. In contrast to the linear cellulose, starch forms a helix due to its alpha-glycosidic bond, which results in fundamental material differences. The previously mentioned isosorbide is a derivative prepared from starch. Dextrin, too, is processed starch by heat and acid to hydrolyze the polysaccharide in smaller fragments. These fragments undergo a repolymerization and result in a highly branched polymer with good solubility. Dextrins are classified by their solid contents and with respective increases in their molecular weights as canary dextrins, white dextrins, and British gums, the latter possessing the strongest adhesive of these three types. To improve the water resistance of waterborne bio-based starch adhesives is a challenging task. The dry strength of such adhesives is fairly high, but exposure to high moisture causes a significant decrease in "wet strength" (Kumar Patel et al. 2013). Treatments with phenolic compounds like caffeic acid and chitosan indicated promising results. Also a system based on modified starch and chitosan limited the water solubility of the starch adhesive (Karak 2016).

Potential of Blends, Gum Dispersions, and Exopolysaccharides

In the context of intermediate or complete bio-based adhesives, different attempts have led to successes by blends of (i) corn starch with tannins, as substitute for phenol in the resin to get closer to formaldehyde-free wood adhesive, (ii) vinyl acetate grafted onto starch and combined with silica nanoparticles to improve water resistance and physical properties of the binding, (iii) and phenol-formaldehyde with fermented biomass, a co-product from ethanol production, comprising glycocalyx, adherent bacterial cells, and fibers (Kumar Patel et al. 2013). Blends of xylan derivatives with dispersing agents as poly(vinyl alcohol) or poly(vinyl amine) and addition of cross-linkers gave a potential wood adhesive as well.

Gums are exudates that are sweated out as a result of injuries to plant parts (e.g., bark) and solidify in air. Gums consist of hydrophilic and hydrophobic heteropolysaccharides with colloidal properties. Gums are suspension and emulsion stabilizing compounds as they inhibit crystallization. For this reason, they are used in hairsprays or in foods such as ice cream and jellies. Common gums are gum arabic, gum tragacanth (spermicidal gels), gum ghatti (enhanced oil recovery, explosive additive, and wax emulsifier), gum karaya (denture adhesive cream due to high wet adhesive strength), and guar rubber (explosive additive, “fracfluid” additive).

Gum dispersions are heat resistant and possess an intrinsic tack. They are used in plaster adhesives, pressure-sensitive tape and dentures, paper adhesives, pharmaceutical tablet binders, and label pastes. Locust bean gum additionally exhibits excellent water resistance. The binding is comparable to D2 wood adhesive like poly(vinylacetate). Also comparable to this standard were some candidates of investigated microbial polysaccharides in a study of bacterial derived wood adhesives, except for xanthan (which was also successfully tested for wood applications in a different study); candidates included among others photo-curable dextran urethanes, exopolysaccharides from periphytic marine bacteria and from *Bacillus megaterium*, and pullulan (Karak 2016).

54.2.5 Protein-Based Adhesives

Three thousand five hundred years and most likely even longer ago, proteins from milk, egg white, and blood were intuitively used as binders and additives in construction materials. Proteins consist of amino acids which differ in their residues. Depending on their composition, they can be tailored for different purposes ranging from catalysis (enzymes), structuring (collagens), transport (ionic channels, hemoglobins), communication (hormones), protection (immunoglobulins), fixation of nitrogen (nodule bacteria), and movement (actin). Gluten (Latin *glūten* for glue) from wheat is a combination of gliadin (56%, responsible for viscosity due to its low molecular weight) and glutenin (44%, quaternary structures with molecular weights >1000 kDa), in sum an elastic storage protein with exceptional adhesive characteristics. It is the main component beyond water in seitan (meat substitute). Gluten is chiefly used in the baking industry but also in the paper industry, and furthermore as an additive in concrete and mortar, and in adhesives. A protein that obtained significant interest is casein, maintained from milk by lowering the pH; it was already used as paint in caves to bind pigments. It is also known as thermoset, namely, galalith, when cured with formaldehyde. The water resistance of casein paints can be achieved by adding chalk milk to it. Because of the food competition and its high price, casein was replaced widely. Still, it is used even today in the food sector for printing casein inks on sausage casings or for labeling bottles. Indoor paintings and paints in kindergartens are also often casein based (Türk 2014). Casein fibers have most comfortable, excellent water transportation, air permeability, and long-lasting antibacterial effects and have received valid international certifications for ecological textiles. These characteristics are attractive for the fashion sector, but in medical applications they were considered cytotoxic.

As a plethora of interesting, proteinaceous structures exists and corresponding unique properties have been identified, the areas of applications as adhesives have rapidly become extremely complex, as the following review focused on just the three major classics beyond casein shows. Treatment of the marine adhesive proteins is postponed and covered in the section polyphenol-based and bioinspired adhesives.

Fibrous Proteins (Collagen, Animal Glues, and Fish Glue)

Collagen, keratin (wool), silk, and elastin are common fibrous proteins. As structuring molecules some of them are constructed hierarchically just like cellulose. Without pretreatment they can be used as reinforcing agents. Collagen is a by-product from leather manufacturing and is used in foods, pharmaceutical products, and medical devices (wound dressing and tissue engineering). In particular medical applications promise a substantial added value.

Animal glues are obtained by boiling bones (bone glue), skin (hide glue) or swim bladders, and skin and bones from fish (isinglass or fish glue). Cartilage glue, on the other hand, is not based on the same compound as other animal glues, but is made up of chondrin, a protein-carbohydrate complex, with less adhesive power (chondroitin sulfate glue). Boiling of the gelatine leads to a water-soluble substance that consists mainly of partially unfolded collagen, whose composition is similar to that of gelatine. All animal glues are high-polymer proteins and derivatives of collagen that form colloids (NPCS Board of Consultants and Engineers 2017).

Degradation, e.g., by hydrolysis and heating of collagen (mainly type I), results in gelatine, which was already used by the ancient Egyptians as an adhesive. Gelatine is able to swell and to absorb water due to a high content of polar residues (about 65%). It is amphiphilic, which makes it suitable as an additive to stabilize foams (Türk 2014). The sum of excellent properties inaugurates versatile niche applications as, for example, in stucco work as a gypsum additive (delaying hardening and increasing strength), in gas masks as an antifogging additive, in compostable candles on graves, and in gum blends as a smoothener and as barrier adhesive. Currently the price for gelatine is relatively low compared to that of synthetic or plant proteins.

Proteins in Tissue Engineering

Substrates involved in surgeries are challenging substrates that require advanced adhesives and need to obey certain natural concepts: fibrinogen and fibrin are proteins present in blood plasma (see chapters in von Byern and Grunwald 2010) and so is albumin, which is inter alia located in the blood. Both and furthermore collagen possess remarkable properties and excellent biocompatibility. Therefore they are used as medical adhesives with FDA approval (albumin limited to surgical repair of acute thoracic aortic dissections). Albumins are globular proteins with amphiphilic character and a high content of the sulfur containing amino acid cysteine. They have polar domains exposed to the outer site, while the lipophilic ones are directed to the inner sphere. This structural feature enables them to function as transporters of water-insoluble compounds. Albumin-based adhesives are usually cross-linked with glutaraldehyde or similar organic compounds and reach an initial tack in about 30 s. Their bonding strength becomes maximal within a few minutes and ranges between 10 and 40 kPa (Bochynska et al. 2016). Fibrin and fibrinogen belong to the blood clotting system. In combination with thrombin, calcium ions, and factor XIII, they are the most commonly used bio-based tissue adhesives, although their bonding strength (approx. 0.01 MPa) is one order of magnitude lower than gelatine-resorcinol-formalin adhesives (approx. 0.1 MPa) (see chapters in von Byern and Grunwald 2010). Collagen and gelatine, a water-soluble derived form of collagen, became integral parts of the surgeon's toolbox as well: its applications are established in tissue reconstruction, e.g., after drastic damage from combustion, owing to the high potential as a surgical sealant. The substrate can be enzymatically cross-linked by transglutaminase and gelates in less than 5 min with bonding strengths about 15–45 kPa. Gelatine is considered biodegradable, non-immunogenic, and biocompatible. It usually needs a cross-linking agent as well as a polymeric additive (e.g., alginate based), with additional functional groups available for cross-links to achieve sufficient mechanical strengths. But it can also be designed as a two-component adhesive such as photochemically induced cross-linking of oxidized urethane dextran and gelatine (Mathias et al. 2016).

Vegetable Proteins

Vegetable proteins like those of soybeans, maize, peas, or wheat gluten, as described above, are in principle all suitable for adhesion applications. As raw materials of by-products, they bear potential for sustainable substitutes, e.g., in wood adhesives. In contrast to casein, they benefit from mild hydrolysis (enzymatical or chemical) or physical treatment to alter their molecular structure by unfolding into a suitable conformation for adhesional processing. Due to its comparatively low costs and good adhesion characteristics, soy protein has established itself as a binder for fillers and pigments in (paper) coatings. Thus, it gives paper a glossy white surface. It was already used in the USA until the beginning of the last century as a low-budget (0.02 dollar/pound; Weakley and Mehltretter 1965) adhesive composed of soy protein, a nonvolatile starch dialdehyde, and lyophilized blood. Just cross-linked soy proteins are not suitable as pure material; they need to be blended with plasticizers because of their brittleness. Also the water content has a considerable impact on the material properties. Up to now just 0.5% of soy protein is used in industrial applications (Türk 2014).

Nevertheless, strength and water resistance of vegetable proteins are still far removed from commercial adhesives. Their potential, however, can be increased by blending them with poly(vinyl acetate) or poly(vinyl alcohol) but also with other proteins as described for the American low-budget formulation with blood and casein (Mathias et al. 2016).

54.2.6 Polyphenol-Based Adhesives

Polyphenols are natural compounds found in animals and plants. These bulky molecules comprise an aromatic p-system and hydroxyl groups in phenolic groups like catechols. It is assumed that the catechol functionality is responsible for adhesive and cross-linking characteristics. In plywood industry the most common adhesives are phenol based and cross-linked by formaldehyde (phenol-formaldehyde). It stands out with excellent weather and water resistance. Based on the structural similarity, several attempts have been made to replace phenol by lignin derivatives. Lignin is composed out of p-coumaryl alcohols, coniferyl, and sinapyl. These three phenylpropanoid monomers give an amorphous polyphenol linked via a multitude of interunit bonds. Lignin is linked covalently to hemicellulose. It serves as a waterproof and antimicrobial binder for cellulose fibers in wood and is a highly valuable by-product of the lignocellulosic bio-refinery and pulping industry. The latter is less suitable as the lignin coming from the bio-refinery for the use as adhesion. Lignin coming from the bio-refinery has fewer methyl groups and that enhances reactivity. Therefore the lignocellulosic residues have a high content of reactive lignin with access to condensation reactions with phenol and formaldehyde in alkaline conditions. Lignin can replace phenol up to 50% in the formulation (plywood based of such a formulation reached the outdoor grade pursuant to the Chinese National Standard) (Mathias et al. 2016). Homogeneous and constant batches of lignin can also be obtained directly starting from different biomass sources by environmentally friendly enzymatic processes. These enzymes involving laccases, tyrosinases, and lipoxygenases transform lignin into a reactive biopolymer that can be used, e.g., as prepolymers, in adhesives or coatings. A life cycle assessment explored the environmental sustainability of the production. Laccase-modified and reduced lignin-soy protein adhesives yielded more than half of the strength of a common polyurethane adhesive (Mathias et al. 2016).

Adhesives from marine sessile organisms are well designed for hydrated surroundings. Several mechanisms are responsible for this performance, depending on the purpose of shorter- or longer-lasting adhesions. In many adhesives key compounds in the composition could be identified such as the amino acid lysine, in case of the sperm cells from goby fish (Mathias et al. 2016), hydroxyproline, or 3,4-dihydroxyphenylalanine (DOPA). The marine bacterium *Alteromonas colwelliana* uses L-DOPA, tyrosine, and related quinones beyond exo-polysaccharides for moisture-resistant adhesion just like some higher organisms like mussels do. DOPA is very versatile in its reactions that are depicted in Fig. 1. It can act as cross-linker or as initial adherent as well. Due to these abilities to adhere in wet conditions and to build up stable networks, these glues gave inspiration for biomedical applications and other technical uses (see Sect. 4.2).

DOPA is just one representative phenolic compound. Tannins, lignin, urushi, and cashew nut shell liquid (CNSL) are further examples. The shell of cashew nuts contains about 20% of CNSL, which is composed of an allergenic phenolic lipid, mainly anacardic acid (71–82%) and also cardol (4–20%), cardanol (1–9%), and 2-methylcardol (1–4%). Anacardic acid is a potent skin irritant, similar to the allergenic oil urushiol (toxin of ivy). The extraction process causes decarboxylation of the anacardic acid leading to cardanol (Maiorana et al. 2015). The structural increments are related to the properties of the resins, made up of phenolic compounds: (i) hydroxyl groups are responsible for good adhesion and proper reactivity at moderate temperatures; (ii) a long aliphatic side chain gives resistance to water, good anticorrosive properties, low viscosity, long open/application time, and flexibility; and (iii) the aromatic ring ensures excellent chemical resistance.

The oldest adhesive used by mankind, birch tar, is also considered to be a polyphenolic representative. Another well-known tar is bitumen, whose use was documented at the site of Umm el Tlell and Hummal (Syria). It dates back to about 70,000 years to the Middle Paleolithic (Boëda et al. 2008). Even though it cannot be considered as actually renewable, it is a natural petroleum tar, consisting of

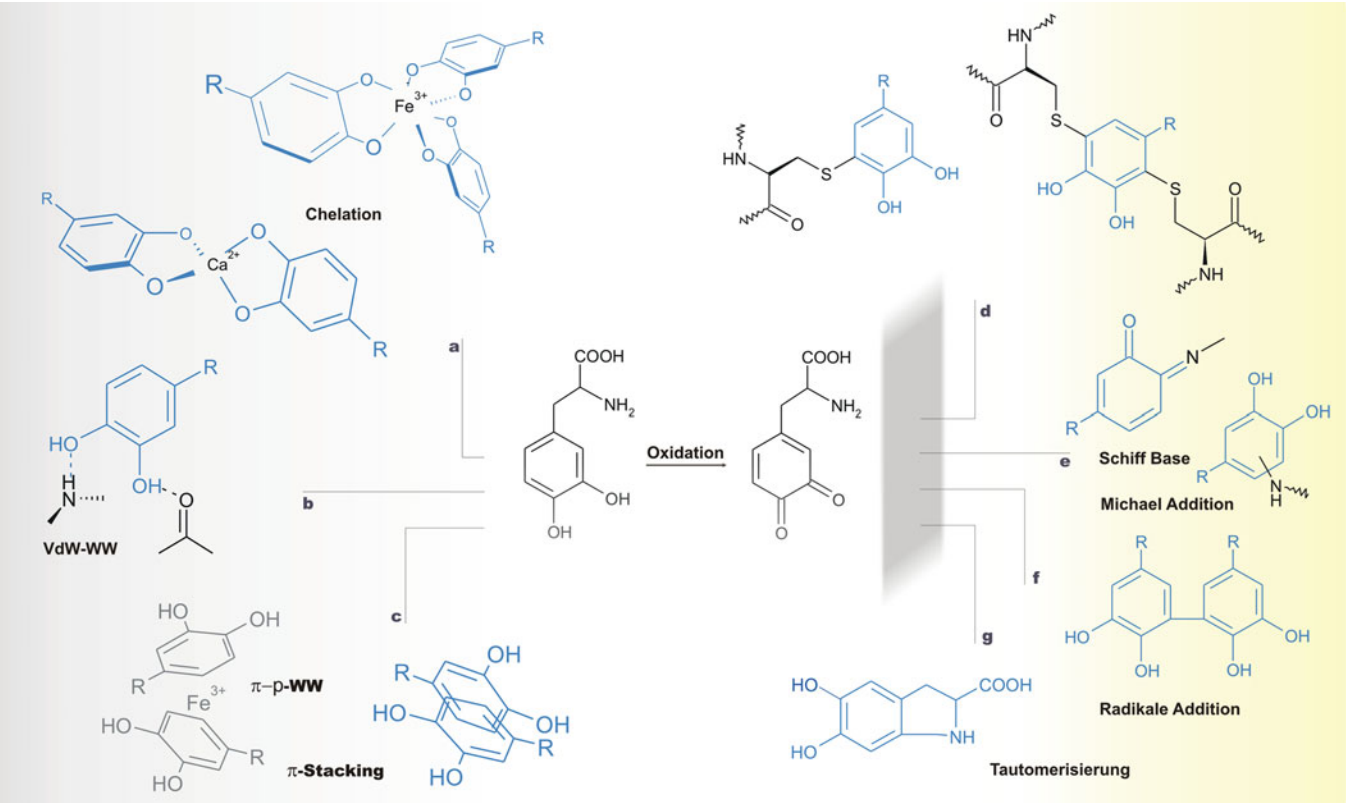

Fig. 1 Catechole can act as chelating ligand and complexate metall ions (**a**), the hydroxy group is capable to interact by hydrogenbridging (**b**), the phenol can use its π-system for interactions with p-Orbitals und π-Orbitals (**c**). Quinone can form covalent bonds by reactions with thiol (**d**); form Schiff Base and undergo a

macromolecular chains that become solid by entanglement without any cross-linking, a natural hot melt. Resins (see Sects. 2.1 and 2.3.1) and tars have widespread uses as adhesives. Bitumen is available in liquid form, as water emulsion or in solvents, and also in solid form like hot melts. Additives like proteins or thixotroping agents are used in bitumen formulations to adjust their viscosity, tack, and mechanical strength. The tack can be improved by an addition of ionomeric elastomers and flexibility benefits from rubber latex in the formulation. Cigarette butts encapsulated with bitumen are used in construction and combine recycling with improving the mechanical properties of asphalt concrete by reducing thermal conductivity. This reduces the feared Urban Heat Island effect and also hot spots on roads caused by sunlight (Mohajerani et al. 2017).

54.3 Biological Adhesives

Bioadhesives from bacteria, plants, and animals have proven their efficacy for 500 million years and become adapted to suit the needs and requirements of the organisms producing them. However, still very little is known about the composition, production, secretion, and mechanical properties of the vast majority of these systems. Generally speaking, biological adhesion tends to be based on two principles:

(i) Attachment via mechanical systems and interfacial forces, i.e., by van der Waals forces or capillary interactions as seen in geckos, flies, beetles, tree frogs, and ivy or by reduced-pressure systems as given in cephalopod suckers (see ▶ Chap. 55, "Biological Fibrillar Adhesives: Functional Principles and Biomimetic Applications"). Among these systems, hairy and smooth toe pads have been studied most extensively, and the structures present on the feet of gecko and tree frog species have become model systems with successful prototypes and applications.

(ii) Usage of chemical bonds based on, e.g., proteins or other macromolecules. These secretions are released through specialized glands and serve not only for solitary attachment and locomotion as for mechanical system but also for other purposes such as construction or defense.

Around 100 marine and terrestrial organisms are known to secrete adhesives (see Graham 2005; Hennebert et al. 2015; von Byern et al. 2018 and contributions in Smith and Callow 2006; von Byern and Grunwald 2010; Smith 2016), but of these only a few organisms have already been characterized in detail or implemented into functional prototypes (see Tables 1, 2, 3, 4, 5). However, as even closely related

Fig. 1 (continued) kind of Michael reaction (**e**) or by radical addition forming a aryl-aryl-coupling (**f**). The DOPA-quinon can also tautomerise to a melanin precursor (**g**) Image from Rischka et al. (2010) and republished with permision

Table 1 Compilation of organisms using biological adhesives mainly for predation (no claim is made to completeness)

Bioadhesive main function	Phylum (zool)/order (bot)	Genus	Glue production	Chemical composition	Bonding properties	Major references
Predation	Ericales, Nepenthales, Lamiales	Carnivore plants (*Drosera*, *Byblis*, *Pinguicula*)	Glue droplet on stalked gland, situated on the leaves	4% aqueous solution of single polysaccharide and chemical elements (Ca, Mg, K, Na)	Viscoelastic (10^2 N·s/m^2), hygroscopic, bonding lost <70% rH	See contribution in von Byern and Grunwald (2010)
	Ctenophora	Comb jelly (*Pleurobrachia*)	Conical cell with spiral filament (colloblast) in tentacles, projected against predators	Histochemical confirmation of basic proteins ($pK_S \approx 8$) and sugars	Not determined (n.d.)	von Byern et al. (2017b)
	Onychophora	Velvet worm (*Principapillatus*, *Euperipatoides*)	Slime gland ducts in body cavity, glue ejected through slime papillae at the head	84–90% water, 55% protein (8–1300 kDa, major protein Er_p1 = 250, 350 kDa), major amino acids Gly (27 mol%) and Pro (13 mol%), 1.3% sugar (mannose, galactose), lipids, no toxin	n.d.	von Byern et al. (2017b) and von Byern et al. (2017a)
	Mollusca	Worm snail (*Vermetus*, *Dendropoma*)	Sticky mucus net, produced by modified pedal gland system	Mucopolysaccharides and glycosylated proteins, toxic components	n.d.	Klöppel et al. (2013)
	Arthropoda	Orb-weaver spider (*Leucauge*, *Araneus*)	Glue droplets on viscid silk capture thread, produced by aggregate glands at abdominal spinneret	Proteins (>65 kDa), major amino acids Gly (22 mol%) and Pro (16 mol%), sugars (N-acetylgalactosamine), lipids, choline, GABamide, isethionate, elements (KNO_3, H_2PO4^-, Na, Cl, Ca)	Resistant to UV irradiation, temperature (18–30°), high humidity range (20–90%), tensile strength 5–32 µN/mm	Graham (2005) and Sahni et al. (2014)

		Fungus gnat larvae (*Arachnocampa*, *Keroplatus*)	Glue droplets released through the mouth and attached to silk threads	Water (99%), proteins (58–62 kDa), chemical elements (P, S, K, Ca), free fatty acids, no sugars	Hygroscopic, bonding lost <80% rH, low bonding strength	
		Spitting spider (*Scytodes*) Bola spider (*Mastophora*)	*Scytodes*: glue and toxin produced in cephalothorax (prosoma) and ejected through cheliceria (mouth area) along a silk thread. *Mastophora*: silk thread with adhesive droplets produced from spinnerets, bola swung against prey (attracted by pheromones)	*Scytodes*: presumably small (3.5–7.0 kDa) glycine-rich and diglutamine-/dityrosine-containing peptides, high amount of toxins *Mastophora*: n.d.	*Scytodes*: contraction and shortening during hardening (force 0.1–0.3 mN) *Mastophora*: low viscosity liquid. Mass of folded threads within the sticky ball	von Byern et al. (2017b), Eberhard (1980), and Yeargan (1994)
		Harvestmen (*Mitostoma*)	Pedipalps with clavated setae, secreting glue droplet	Triglycerides, oleic fatty acids, high water content	Pull-off force 7μN, dehydration, no solubility in 70% ethanol	See contribution in Smith (2016)
		Rove beetles (*Stenus*)	Glands located in the head, sticky labium catapulted toward prey	Proteins, sugars, and lipids	n.d.	See contribution in von Byern and Grunwald (2010) and Koerner et al. (2012)

Table 2 Compilation of organisms using biological adhesives mainly for defense (no claim is made to completeness)

Bioadhesive main function	Phylum (zool)/ order (bot)	Genus	Glue production	Chemical composition	Bonding properties	Major references
Defense	Mollusca	Slug (*Arion*) and snails (*Cornu*)	*Arion*, dorsal foot glands *Cornu*, defensive foamlike secretion, released through mantle cavity	*Arion*, matrilin- and lectin-like proteins, interpenetrating a sulfated polysaccharide network, chemical elements (Ca and Mg) *Cornu*, proteins (30, 50 and >120 kDa) (unpubl.), other molecules and elements not characterized yet	n.d.	See Wilks et al. (2015) and contribution in Smith (2016)
	Echinodermata	Sea cucumber (*Holothuria*, *Actinopyga*)	Sticky Cuvierian tubules, released through cloacal orifice. Glands located in the tubules	60% protein (17–220 kDa), major amino acids Gly (12–30 mol%) and Glx (9–16 mol%) depending on the species, 40% neutral sugar, toxin holothurin	Excreted tubules elongate 20x to original length, sticks within 10 s. Tensile strength >135 kPa	See contributions in von Byern and Grunwald (2010), Smith (2016), and Graham (2005)
	Arthropoda	Chilopoda (*Henia*, *Geophilus*)	Sternal glands (multicomponent system) located on the ventral body side	Two major proteins (12 and 130 kDa); some species additionally contain hydrogen cyanide (HCN); species-specific pH range	Hardening in the moment of release	von Byern et al. (2017b)
		Termites (*Tenuirostritermes*, *Nasutitermes*)	Gland in the head capsule ejects the glue through a modified pore (named fontanellar gun)	*Tenuirostritermes* resin composed of 62% α-pinene, 27% myrcene, and 11% limonene; some species also contain toxins and pheromones	Hardening within 10 s	Nutting et al. (1974) and contribution in von Byern and Grunwald (2010)

	Chordata	Salamander (*Ambystoma*, *Plethodon*)	Milky secretion from dorsal and ventral skin glands (two-component system)	70% water, 78% protein (15–120 kDa), 0.41% sugar (mannose, α-L-fucose, N-acetyl-D-glucosamine), lipids, chemical elements (Na, Cl, K, S); some species secrete distasteful substances with its glue	Hardening within seconds, tensile strength >1.7 MPa (unpubl.), hydrophobic in cured stage	von Byern et al. (2017b) and von Byern et al. (2017a)
		Burrowing ground frog (*Notaden*)	One dorsal skin gland (granular gland)	85–90% water, 55–60% protein (13–500 kDa, dominant Nb-1R), major amino acids Gly (16 mol %) and Pro (9 mol%), 0.75 % sugar	Tensile strength >70 kPa (within 24 h), shear stress >2800 kPA (cured 1 week on wood)	See contributions in von Byern and Grunwald (2010), Smith (2016), and Graham (2005)
		Hagfish (*Eptatretus*, *Myxine*)	Lateral slime glands (two-component system), secreting proteinaceous threads and mucin vesicles	99.9% water, 0.002% thread (proteins) and 0.0015% mucin (acidic sulfated glycoproteins), chemical elements (Na, Cl, K)	Elastic and coherent soft hydrogel, high extensibility. No adhesiveness	von Byern et al. (2017b)

Table 3 Compilation of organisms using biological adhesives mainly for construction (no claim is made to completeness)

Bioadhesive main function	Phylum (zool.)/ order (bot.)	Genus	Glue production	Chemical composition	Bonding properties	Major references
Construction	Arthropoda	Eusocial wasp (*Polistes*, *Vespa*)	Salivary secretion used as binder for organic material to build papery nest. The number of glands varies between species	Species dependent: presumably mostly proteinaceous (>73%, silklike) and insoluble polysaccharides, major amino acids (Ala, Ser, Gly), chemical elements as K, S, Zn, Fe	Water resistant, light weight (thickness 43 μm), tensile strength (0.25–1.02 MN/m^2)	McGovern et al. (1988), Singer et al. (1992), and Cole et al. (2001)
		Honeybee (*Apis*)	Wax glands (three cell types) located ventrally on the 4–7 abdominal segment	Mixtures of wax esters, hydrocarbons, free fatty acids, and alcohols	Mechanical manipulation at 35 °C, melting point at 62–64 °C, fragile at low temperature, not adhesive	Tulloch (1970) and Hepburn et al. (1991)
		Huntsman spider (*Cebrennus*, *Leucorchestris*)	Sticky silk threads secreted from the abdominal spinneret to line and stabilize the burrow in the desert sand	n.d.	n.d.	Foelix et al. (2016) and Henschel (2017)
		Caddisfly larvae (*Hesperophylax*)	Salivary gland secretions (silk and glue coat) as binder for organic/inorganic material constructions Silk as double fiber with 5 μm diameter, core (<100 nm), coating >0.5 μm thick	Silk core: H- and L-fibroin (>350 and 25 kDa); major amino acids Pro, Glu, Cal, Lys; chemical element as Ca Glue coat: neutral and acid glycoproteins, heme peroxidase	Stress 4.5 MPa (pH dependent), elongation up to 120%, recovery bisphasic and Ca^{2+} dependent	See contribution in Smith (2016)

	Annelida	Sandcastle worm (*Phragmatopoma*) Tube worm (*Sabella*)	Four distinct secretory cell types in the building organ release the cement to stick sand grains toward a tube	Proteins rich in DOPA, major amino acids Ser (29 mol%), Gly (26 mol%), Ala (10 mol%)	Tensile strength >2,4 MPa	See contributions in Graham (2005), Smith (2016), Graham (2005), and von Byern et al. (2017a)
	Chordata	Swiftlet (*Collocalia*)	Salivary secretions used as binder or solitary for bird nest building	Two glycoproteins, sialic acid-rich O-glycosylproteins		Oda et al. (1998)
		African lungfish (*Protopterus*)	Three types of goblet cells, which differ morphologically and histochemically Skin secretions form a protective outer cocoon against dry periods in the soil	Positive staining for sugars (PAS)	n.d.	Kitzan and Sweeny (1968) and Greenwood (1986)
		Stickleback fish (*Gasterosteus*)	Nest construction with organic material. Glue produced in the kidney, stored in the urinary bladder	Protein (Spiggin, 203 kDa), major amino acid Cys (8 mol%)	Highly elastic thread, silklike appearance	Van Iersel (1953) and Jakobsson et al. (1999)

Table 4 Compilation of organisms using biological adhesives mainly for attachment (no claim is made to completeness)

Bioadhesive main function	Phylum (zool)/ order (bot)/ kingdom	Genus	Glue production	Chemical composition	Bonding properties	Major references
Attachment	Bacteria	*Pseudomonas*, *Caulobacter*	Extracellular matrix, synthesized by three different mechanisms: ABC transporter, Wzx/Wzy dependent, synthase dependent. Attachment via fimbria/pilus	Adhesin (i.e., FimH) and exopolysaccharides as mannose, N-acetylgalactosamine, rhamnose, etc.	Binding partly effected by acidic pH (4–5), adhesion μN range	See contribution in Smith (2016)
	Fungi	Yeast (*Candida*)	Depending on function (substrate or spore bonding), i.e., appressorium, hyphodium, conidia, epithelial cells	Species-specific macromolecules (Eap1, 110 kDa protein, 90 kDa mannoprotein, etc.), mucilaginous matrix (containing mycosporine-alanine, cutinase, esterase, etc.), sugars (i.e., mannose, galactose)	Appressorium turgor pressure up to 8 MPa and force of 17 μN	See contribution in Smith (2016)
	Ochrophyta	Diatom (*Toxarium*)	Glue secreted through slit in the silica cell wall (termed raphe)	Protein (single >220 kDa), major amino acids (Gly 22 mol%, Asx 14 mol%, His 11 mol%), sulfate, chemical elements as Ca, Mg, sugars (mannose, xylose, etc.)	0.8 nN, self-healing properties	See contribution in Smith (2016)

	Malvales Santalales	Flowering plant (*Tilia*) Mistletoe (*Viscum*)	Pollen: 1. Pollenkitt produced by anther tapetum 2. Viscid thread is part of the ektexine	Pollenkit: lipids, carotenoids, protein Viscid thread: polymer bases on sporopollenin Viscin: polysaccharide only	Viscid threads are flexible but not elastic threads	See contribution in von Byern and Grunwald (2010)
	Asparagales	Orchid (*Catasetum*)	Viscid disc, attachment of pollinarium to pollinator. Temporary attachment	Glycoprotein including sucrose, glucose, fructose	n.d.	Schlee and Ebel (1983)
	Alismatales	Arrowhead vine (*Syngonium*)	Aerial root hair, permanent attachment to all types of substrata	Proteins and polysaccharides	n.d.	Yang and Deng (2017)
	Apiales	English ivy (*Hedera*)		Arabinogalactan proteins, pectic polysaccharides, chemical element (Ca)	Combination of physical contact, chemical secretion, and shape modification. Tensile strength, 3.4 MPa (single root hair)	Melzer et al. (2010) and Huang et al. (2016)
	Ulvales	Sea lettuce (*Ulva*)	Vesicles with adhesive content in free-swimming zoospore	Protein (110 kDa), glycan moieties	Vesicle discharge and curing within 1 min, Ca^{2+} involvement	See contribution in Smith and Callow (2006)
	Laminariales	Giant kelp (*Macrocystis*, *Durvillaea*)	Vesicles (physodes) released from fertilized zygote for permanent attachment	Phlorotannin with phloroglucinol monomer. >150 compounds with MW from 126 Da to 650 kDa, cross-linked Ca alginates	Tissue adaptation, thallus breakage, shear stress >0.3 MPa	See contributions in Stevens et al. (2002), Smith and Callow (2006), and Graham (2005)

(*continued*)

Table 4 (continued)

Bioadhesive main function	Phylum (zool)/ order (bot)/ kingdom	Genus	Glue production	Chemical composition	Bonding properties	Major references
	Porifera	Demosponge (*Lubomirskia*)	Baso-pinacocyte secreting spongin for permanent attachment. Chitin glands not determined yet	(a) Spongin (collagen-like protein) (b) Chitin (close to α-chitin)	n.d.	Evans (1977) and Ehrlich et al. (2013)
	Cnidaria	Freshwater polyp (*Hydra*) Beadlet anemone (*Actinia*)	Gland cells at the basal disc part of the peduncle for temporary bonding	*Hydra*: proteins (presumably glycosylated), protein characterization in progress *Actinia*: 96% water, 24% protein (12-200 kDa), 8% carbohydrate, 1% lipid, 67% chemical elements (Cl, Na, Mg), equinatoxins	Muscle-mediated detachment	Stabili et al. (2015) and Rodrigues et al. (2016)
	Mollusca	Mussel (*Mytilus*)	Byssus threads with distal adhesive plaque, originated from glands in the foot organ. Permanent bonding but mobility given by thread breakage and re-anchorage	6 foot proteins (115, 42–47, 5–7, 79, 9.5, 11.6 kDa) with different amounts of DOPA, collagenous core	Mussel plaque tensile strength >0.85 MPa (with seasonal variation), plaque area varies to surface energy	See contributions in von Byern and Grunwald (2010), Smith (2016), and Graham (2005)
		Violet sea snail (*Janthina*)	Anterior part of the foot (propodium), mucus used as float, >12 cm long, >2 cm width	n.d.	Quick curing. Enclosure of gas to a foamlike buoy. Clear glue color	Laursen (1953)

		Cephalopoda (*Nautilus*, *Idiosepius*)	Adhesive glands on digital tentacle (*Nautilus*), dorsal mantle (*Idiosepius*), other body regions. Temporary attachment	Histochemical confirmation of acidic (1.0–2.5) and basic proteins (pH $\approx$ 8.0) and sugars	Weak bonding, fast release, for some species a mechanical detachment is assumed	See contribution in von Byern and Grunwald (2010)
	Platyhelminthes	Flatworm (*Macrostomum*)	Adhesive organ at the tail. Duo-gland system (one gland for attachment, other for release). Temporary attachment	Proteins (characterization in progress) and carbohydrates (PNA lectin); transcriptome	n.d.	Lengerer et al. (2016) and Lengerer et al. (2017)
		Ectoparasite (*Entobdella*)	Anterior adhesive pad with two gland types, with rod- or spheroid-like content	Protein, lack of sugars, lipids, and L-DOPA, similarities in amino acid composition to sea star, limpets, and barnacles	Cement-like glue, resistant to shear force from water current, temporary bonding	Kearn and Evans-Gowing (1998) and Hamwood et al. (2002)
	Arthropoda	Ticks (*Dermacentor*, *Amblyomma*)	Salivary gland. Used as temporary attachment in the skin as a dowel	Two proteins (RIM36, 64P), major amino acids Gly, Pro, Tyr. Proteins similarity to keratin, collagen, glutenins. Protein 64 P homology to *Phragmatopoma* (see Sect. 3.3)	Glue with quick-hardening core and slow-hardening cortex, high bonding strength	Kemp et al. (1982), Graham (2005), and Hennebert et al. (2015) Johannes
		Acorn barnacle (*Balanus*, *Megabalanus*)	Unicellular gland type in the body secrete cement for permanent bonding	84–90% protein (majors from 16- 110 kDa), 1% sugar, major amino acids Ser (9–11 mol%), Leu 8–9 mol%), Pro (8 mol%)	Tensile strength >2 MPa (cyprid larva and adult)	See contributions in Smith (2016), Graham (2005), and von Byern et al. (2017a)

(continued)

Table 4 (continued)

Bioadhesive main function	Phylum (zool)/ order (bot)/ kingdom	Genus	Glue production	Chemical composition	Bonding properties	Major references
		Goose barnacle (*Lepas*, *Dosima*)	Unicellular gland type in the stalk. Cement used as attachment and by *Dosima* also as buoy	*Dosima*: 92% water, 84% protein (60–85 kDa), major amino acids Ser (6–9 mol%), Gly and Ala (10 mol%), Leu (8–10 mol %), 1.5% sugars	Gas volume 19%, hardness 2.5 kPa, tensile strength 0.2 MPa	Zheden et al. (2015) and von Byern et al. (2017a)
		Stoneflies (*Dinocras*) Fruit fly (*Drosophila*) Sphecoid wasps (*Liris*)	Egg anchorage on substratum or prey: *Dinocras*: follicle cells with ovaries *Drosophila*: abdominal gland *Liris*: tubiform Dufour gland on the abdomen	*Dinocras* and *Drosophila*: protein, polysaccharide *Liris:* proteins (14–200 kDa, straight-chain hydrocarbons as pentadecane, (Z)-8-heptadecane	n.d.	See contribution in von Byern and Grunwald (2010)
	Chaetognatha	Arrow worm (*Spadella*)	Some species bear adhesive structures (appear as long rigid fingerlike processes) ventrally in the tail area. Temporary attachment	n.d.	n.d.	Michel (1984)

Table 5 Compilation of organisms using biological adhesives mainly for locomotion (no claim is made to completeness)

Bioadhesive main function	Phylum (zool)/ order (bot)	Genus	Glue production	Chemical composition	Bonding properties	Major references
Locomotion	Ochrophyta	Diatoms (*Crasopedostauros*, *Pinnularia*)	Glue secreted through slit in the silica cell wall (termed raphe), gliding effected through actin filament	Extracellular polymeric substances (EPS) containing mostly sugars (mannose, glucose, galactose). Major amino acids (Gly 18 mol%, Ser 22 mol%, Thr 12 mol%)	Gliding speed >25 μms-1, thickness >150 nm	Poulsen et al. (2014) and see contribution in Smith (2016)
	Porifera	Demosponge (*Tethya*)	Filamentous podia with three distinct gland types, formation of adhesive discs and central fiber	Mucopolysaccharides (not specified)	Movement up to 5–8 cm/week. Bonding to hard substrata	Fishelson (1981)
	Mollusca	Gastropods (*Cornu*, *Patella*)	Mucus released by numerous glands in the pedal sole (ventral body side)	Species-specific: protein (25–50%, mostly pH 1–4, 20–220 kDa); major amino acid Gly (13 mol %); sugar (i.e., mannose, fucose) composition; elements (Cl, K, Ca, S); saturated fatty acids as myristic, palmitic, and stearic acids; water content >93% (in limpets)	Tensile strength >518 kPa	See contributions in Smith (2016), Graham (2005), and Graham (2005)

(*continued*)

Table 5 (continued)

Bioadhesive main function	Phylum (zool)/ order (bot)	Genus	Glue production	Chemical composition	Bonding properties	Major references
	Echinodermata	Sea star (*Asterias*)	Two types of secretory cells (one adhesive, one de-adhesive) in the tube foot Detachment enzymes ensure the glue breakage for foot release	21% protein (one major protein Sfp1), major amino acid Gly (10 mol%), 8% sugar	Tensile strength >198 kPa	See contributions in Smith (2016) and Graham (2005)
		Sea urchin (*Paracentrotus*)		6.4% protein (inter alia nectin and cohesive proteins), 2.5% lipid, 1.2% sugar, large inorganic fraction (45.5%)	Reversible adhesion through release of proteases and glycosylases, glue remains as footprint, tensile strength 340 kPa	Lebesgue et al. (2016) and contributions in Smith (2016) and Graham (2005)

Fig. 2 Biological adhesives used for different purposes such as for protection (1 barnacles), locomotion (2 starfish), defense (3 sea cucumber), and attachment (4 mussels)

species can differ with regard to gland morphology and/or adhesive composition and the secretions have become optimized for different purposes or environments, there are still a huge number of species whose adhesive secretions have not been investigated yet.

Biological adhesives are not exclusively used for settlement, but often also fulfill other purposes in connection with defense, predation, locomotion (Fig. 2), or nest construction and are superbly adapted morphologically, chemically, and physically to the needs and requirements of the organisms that produce them. Different from man-made synthetic systems, biological adhesion works over a wide range of temperatures, in different environments (aquatic, terrestrial, subterranean, arid), and under changing physicochemical conditions. Bonding can occur irrespective of texture or biological interference within milliseconds to all sorts of surfaces, be they natural, synthetic, biological, hard, or soft and with irregular or of complex substratum chemistry. Some organisms form permanent bonds for predation, attachment, or constructions; others use temporary adhesives to enable a holdfast on demand or for locomotion.

This diversity of organisms and variety of adhesive systems as well as the low amounts of secretion available make bioadhesion research challenging, but with access to advanced technological approaches, considerable progress in its characterization has already been made.

In particular most animal-based biological adhesives have been found to be typically polymers, formed by proteins and polysaccharides, which provide robust cohesion strength between the molecules and strong interaction with the contact area. In most animal glues, a high protein content is present (up to 90%), and technical progress has been made in some species, reaching full-length sequences of key proteins involved (Hennebert et al. 2015).

For many other biological adhesives listed in the tables below, a rough estimation of protein number, molecular mass (i.e., 4–650 kDa), and major amino acid residues (in particular serine, glycine, proline, and/or leucine) are available. Difficulties still appear in view of the carbohydrate characterization, as many adhesives contain a relatively low sugar fraction (<3% dry weight) (von Byern et al. 2017). For a few species, glycosidic protein bonds have been characterized in detail (Hennebert et al. 2015), and for most of the others, information on their sugar residues through lectin affinity tests is available. To the best of our knowledge, to date lipids have only rarely been characterized in adhesive secretions (e.g., permanent adhesive of barnacle larvae; Gohad et al. 2014). There is also some information available on the presence of chemical elements such as calcium, zinc, and iron. These kinds of ions serve as cross-linker and stiffen the protein-polysaccharide complex. Rare amino acids such as L-DOPA (L-3,4-dihydroxyphenylalanine) is prominent in the literature being the best characterized key compound in marine adhesive proteins but has been confirmed only in a few marine species (*Mytilus*, *Phragmatopoma*, *Sabella*). Beyond bioadhesion, L-DOPA also plays an important role in insect cuticle sclerotization and mechanical stability of cephalopod beak and polychaete jaws (Miserez et al. 2008).

Despite these technical obstacles, the natural biodiversity is clearly a blessing from a bio-prospecting perspective, providing countless opportunities to identify commonalities and functional principles, thereby developing a better understanding of adhesive mechanisms, evolutionary origins, and adaptations to specific environments and tasks. The key to unlock bioadhesion principles lies in comparative analyses with innovative research approaches based on intellectual and technical exchange as given by EU network projects such as COST Actions TD0906 and CA15216.

54.3.1 Predation

For prey capture through passive trap mechanisms, the glue is initially secreted externally and then attached as droplets or coating on silk threads (e.g., orb-weaver spider *Araneus* and fungus gnat larva *Arachnocampa*), a mucus web (worm snail *Vermetus*), tentacles (comb jelly *Pleurobrachia*), leaves (carnivorous plants *Drosera* and *Pinguicula*), or other prey capture devices. These traps are mostly exposed for days to weeks to varying habitat conditions (UV radiation, humidity, temperature, salinity, wind, rain) but still exhibit a bonding ability at prey contact. To minimize prey escape, the glue-containing parts are closely arranged to increase the number of contact points and to ensure that the tangling prey is rapidly entrapped by the sticky secretion. Observation in *Pleurobrachia* indicates that the animals could discard too large prey items (von Byern et al. 2018) and also for *Arachnocampa* a defined breaking mechanism is discussed (von Byern et al. 2018). Orb-weaver spiders are known to cope with large prey items by forming high tensile silk threads (up to 0.5 GPa for the viscid silk) (Gosline et al. 1999). Gluing traps in animals/plants are not reused; instead new threads/leaves are formed and exposed. In carnivore plants like *Drosera* and *Pinguicula*, the prey is lured by glistering droplets and optic or odor signals (see respective contribution in von Byern and Grunwald 2010), while the cave-dwelling *Arachnocampa* attracts the prey by a specific light organ (Meyer-Rochow 2007). Also in view of their chemical compositions, the different biological adhesives vary strongly, being often highly adapted to specific habitat conditions and prey (or predator) type as recently shown for *Arachnocampa* (von Byern et al. 2018).

A few arachnid species as *Mitostoma* are known to actively capture prey by means of adhesives. While *Mitostoma* directly attaches the prey with its pedipalps, *Scytodes* and *Principapillatus* expel its secretion from a certain distance (up to 2 cm in *Scytodes* or 4 cm in *Principapillatus*) and within milliseconds onto the prey. Both use canalized structures in the head region (slime papillae, chelicerae) to build up a certain pressure and to control the flow direction (von Byern et al. 2018). Up to two separate jets are used, which run a zigzag pattern over the prey and substratum. Immediately after its release, the glue hardens and partly shrinks to tightly entangle the prey. The predators are able to control the glue amount and use more spit, if the prey is still struggling. While in *Scytodes* the glue is released with silk threads, in *Principapillatus* the ejected glue appears as translucent threads but does not contain silk. It remains questionable if the *Scytodes* glue is toxic itself, but it is known that the trapped prey is paralyzed by injecting toxin afterward. The glue of *Principapillatus* lacks a toxin, so instead digestive saliva is released with a bite to immobilize the prey. In addition to the prey capture, *Principapillatus* also uses its glue for defense against predators.

54.3.2 Defense

Besides, also other species are known to use adhesives as defense. However, while being very effective against the predators, it yet remains unclear for most of these species how they avoid being trapped by its own sticky secretion. Most of these secretions are located in particular epithelial glands (i.e., dorsally in the slug *Arion subfuscus* and burrowing ground frog *Notaden*, ventrally in chilopods as *Henia* or specific body regions in salamanders as *Plethodon*) (von Byern and Grunwald 2010; Smith 2016) to ensure a fast release onto the body surface.

Sea cucumber as *Holothuria* in contrast expels sticky threads (named Cuvierian tubules) when stressed by a predator (see respective contribution in von Byern and Grunwald 2010; Smith 2016). Termite soldiers as *Tenuirostritermes* fire their secretion in large distance (>3 cm), while spitting spiders and onychophorans (see paragraph in Sect. 3.1) use an oscillating behavior toward the predator or prey. Helicid snails as *Cornu* not only retract in their shell to protect themselves from predators but also secrete a foamlike slimy secretion through the shell opening. The defensive glue of the American slug *Arion subfuscus* is formed by the matrilin-like proteins, heparan sulfate-like polysaccharides, and metal ions and currently used as template for medical sealant (Li et al. 2017).

Although the secretion of the hagfishes as *Eptatretus* is not adhesive (von Byern et al. 2018), the mucus they release from lateral skin glands strongly swells and clogs the gills and mouths of the predators. In general, the most defensive secretions are released during contact with the pesterer and dispersed over its body and in particular mouth only a few fires directly toward the predator. Exposure to air causes in *Henia*, *Tenuirostritermes*, and *Plethodon* an immediate hardening of the glue (von Byern et al. 2018), while the adhesives of *Arion*, *Cornu*, and *Eptatretus* remain viscoelastic for a certain time (von Byern et al. 2018; Smith 2016). The Cuvierian tubules in *Holothuria* in contrast remain sticky and form a large web, entangling the predator. In many defensive secretions (sea cucumber, salamander, chilopoda, termites), also toxic, distasteful, or noisomely components could be determined, serving to distract the predator additionally (see respective contribution in von Byern and Grunwald 2010; Smith 2016 von Byern et al. 2018 as well as Nutting et al. 1974), while other bioadhesives (e.g., *Notaden*, *Plethodon*) confirm its biocompatibility in cell culture and medical tests (see Sect. 4.2).

54.3.3 Construction

Biological adhesion and mucus are mainly used as binders for constructions incorporating inorganic/organic materials; a few species also use the secretions for other functions. Annelids as the sandcastle worm *Phragmatopoma* and the tube worm *Sabella* build permanent tubes, in which they reside (see respective contributions in Smith 2016). As given for mussels (see below), also these annelids use the amino acid L-DOPA as binder to stick the sand grains together and by this form strong and stable tubes (up to 40 cm) (Smith 2016). As the animals lift themselves from the soil with increasing tube length and thereby lose the possibility to uptake new construction material from the ground, suspended sand grains are collected, selected, and used for tube repair and partial increase.

In relation to sabellids, other animals form with their secretions temporary architectures. Stickleback fish as *Gasterosteus* build in the spring a tunnellike nest of plant origin for breeding. The threadlike glue is secreted from the kidney and dispersed by the fins on the nest material (Van Iersel 1953). Caddisfly larvae and hunting spiders combine silk and adhesives to form stabile cases/burrows; however, differences are given in the production site. The hunting spider *Cebrennus* releases the sticky silk threads from its abdominal spinneret to line and stabilize the burrow in the desert sand (Foelix et al. 2016). The caddisfly larva instead secretes its silk and glue from the salivary glands and uses all kinds of inorganic and organic material to build portable or substrate-bonded cases; some species even design multilevel cases. Most caddisflies are not as selective as the sabellids (see above) in view of its construction material and case design; some species use all types of material and design their bizarre-looking cases.

Salivary liquid and organic material is also used by social wasps as *Polybia* and birds (i.e., *Delichon*) as nest-cementing substance (Oda et al. 1998). Although the nest constructions may not appear as stable as the caddisfly case, the papery constructions of wasps are quite long-lasting (even after the inhabitant leave) and have very good stability and even water-resistant properties (McGovern et al. 1988). Besides its binder function, adhesives are also solitary used for constructions. Swiftlets build with their concentrated salivary breeding nests (also known as Edible bird's nests), while the African lungfish *Protopterus* (Greenwood 1986) form with its mucus protective cocoons to survive dry periods. The waxlike secretion of honeybees provides not only the basis for the honeycombs in nature but is also commonly used in cosmetics, food, and pharmaceutical industry. Besides bee wax, also other secretions as fish slime (Antony 1954, see Sect. 2) and the *Phragmatopoma* adhesives are known to have a high potential for medical applications, e.g., in the field of fetal membrane defect sites (Mann et al. 2012; Papanna et al. 2015) and spina bifida repair (Papanna et al. 2016) (see Sect. 4.2).

54.3.4 Attachment

The usage of adhesives as a support for surface bonding is surely the most common purpose, used by bacteria, plants, and animals. Especially aquatic organisms use such secretions to withstand currents and avoid drifting. Some seal themselves or their eggs permanently to the substratum or biological surfaces (i.e., *Ulva*, *Macrocystis*, *Lubomirskia*, *Mytilus*, *Balanus*, *Lepas*) and developed cement-like binders with high adhesive strength (up to 2 MPa), adapted to the strong hydrodynamic forces typical of the intertidal regions. Others like *Hydra*, *Nautilus*, *Idiosepius*, *Macrostomum*, *Entobdella*, and *Spadella* adhere only temporarily, "on demand." Detachment is presumably achieved mechanically through muscle contractions or body movements except for the case of *Macrostomum*, where a second gland type (so-called duo-gland system) secretes a detachment enzyme. *Janthina* and *Dosima* release a foamlike glue, enabling them to float on the water and in the water flea *Simocephalus* (Meyer-Rochow 1979); suction in combination with an adhesive may be employed for temporary attachments.

Terrestrial and in particular epiphytic plants (*Syngonium*, *Hedera*) use adhesives for attachment; furthermore a large number of flowers use pollenkitt or viscid threads for pollen binding and transport (*Catasetum*, *Tilia*, *Viscum*). Many insects as *Dinocras*, *Drosophila*, and *Liris* in particular use glues for egg anchorage; animals itself in particular use mechanical tools (see ▶ Chap. 55, "Biological Fibrillar Adhesives: Functional Principles and Biomimetic Applications") for attachment and bonding. Ectoparasites as *Entobdella* or ticks (*Dermacentor* or *Amblyomma*) secure themselves in the host tissue with an adhesive called cement. The cement portion is secreted after insertion of the mouthparts and solidifies almost immediately to tightly anchorage the animal in the tissue during the feeding phase (Kemp et al. 1982). The secretion of the second portion takes up to several days. After feeding, ticks detach from the cement cones, which remain attached in or on the host's skin (Kemp et al. 1982; Suppan et al. 2017).

54.3.5 Locomotion

Also the here listed animals use glue or mucus to bond temporary to the substratum as given for temporary bonding species (see Sect. 3.4). However, the glue is synthesized and released mostly through structures, specialized for locomotion, i.e., the podia of *Tethya*, the gastropod pedal sole, or the tube foot of sea stars and sea urchins. Best known are surely the gastropods, which produce a highly effective, hydrogel-like mucus, enabling the animals to cross any smooth, sharp (razor blades), and even extreme superhydrophobic, anti-adhesive surfaces as polytetrafluoroethylene (PTFE, commonly known as Teflon) (Shirtcliffe et al. 2012). The mucus acts as glue, allowing the animals to adhere and push themselves forward mechanically by means of wavelike movements of the sole (Miller 1974). In contrast, *Paracentrotus* and *Asterias* likewise use a duo-gland system as *Macrostomum* (see Sect. 3.4), in which one gland produces the glue and another secretes enzymes to break the bonding and enable movement. In particular the viscous gastropod mucus and its bonding ability on any surface make this secretion interesting not only for new bioinspired wound sealants (Li et al. 2017) but also to design anti-adhesive surfaces for medical implants and superhydrophobic paints (see Sect. 4.1).

54.4 Bioinspired Applications

Despite the diversity and superiority of biological adhesives (biocompatible, biodegradable, lack of heavy metals, or absence of volatile organic compounds), synthetic adhesives in particular (e.g., phenol/resorcinol/urea-formaldehyde) dominate today's adhesive market and are used as ingredients in many sealants, furniture products, and cosmetics.

Although many synthetic adhesives offer necessary features for specific applications such as for wood manufacturing or in microelectronics, as well in dentistry, their performance is far from optimal and they can have unacceptable properties with respect to their suitability as an essential biomedical tool (harmful, toxic, not biodegradable, low adhesive strength, microbial contamination). Technological advances in the area of superior bioinspired materials have been made with scientific progress in biological adhesion, e.g., the ability to produce key elements like L-DOPA recombinants. Such key components enabled the development of tissue adhesive like Cell-TakTM (USA), the first example (year 1986, TM-No. 73604754) of a marine-derived sealant, based on mussel adhesive proteins only; other biomimetic analogues are currently in the research focus. As a result of our increased understanding of the interrelationships between biological adhesives and underlying mechanisms or similar boundary conditions, it is increasingly possible to transform this into biomimetic solutions. In contrast to the desired copies in the field of bonding according to biological models, these perfectly adapted organisms cause extensive economic loss due to their adhesive powers. For this reason, the progress made in the course of clarifying adhesive phenomena also serves not least to prevent fouling.

54.4.1 Antifouling

Bacterial biofilms are prevalent and possess benefits and damage at once. They cause problems, e.g., by inducing biocorrosion and biofouling in drinking water supplies, and they are liable for impaired safety in surgery and wound healing. But they are also used for waste water treatments (van der Kooij and Van der Wielen 2014). In contrast to nonadherent bacteria, these microorganisms use biofilms as matrices for cooperation and to establish synergistic interactions like preventing the washaway of enzymes and nutrients or in order to survive in hostile environments. Biofilm formation allows them to withstand periods of starvation by quorum sensing. Consequently the vast majority of microorganisms exist in nature in the form of biofilms. They adhere mostly on wet solid surfaces. Within the process of biofilm formation, several steps are distinguished, whereby the first two are interesting in terms of bioadhesion: (1) adsorption to the substrate by cell adhesion (this initial step can last from a few minutes to one hour of exposure and is based on proteins) and (2) formation of extracellular polymeric substances (EPS) composed of polysaccharides to achieve irreversible attachment by polymer bridging (Vandevivere and Kirchman 1993). A well-known example for bacteria attached to teeth and aggregated in a self-made hydrated polymeric matrix is dental plaque.

Micro- and macrofouling (Fig. 3) are causes of considerable economic damage. A 5% increase in biofouling has been shown to increase ship fuel consumption by 17%, with a 14% increase in greenhouse gas CO_2, NO_x, and SO_2 emissions. Biofouling of marine energy turbines is regarded as the primary and most persistent source of failure among these devices. Control of biofouling for aquaculture and fishery operations can account for up to 15% of total annual operating costs. Beyond that is biofouling of sensors a significant barrier to technology advancement due to the impact on data quality (Chapman et al. 2014). Consequently, preventive measures are a challenge for material science. To avoid biofouling is inter alia the purpose for the findings on the principles of action of biological adhesives. Different approaches ranging from the use of “confusing surfaces” – to prevent (micro) organisms from adaption – like dendrimer-based coatings to antimicrobial concepts or surface modifications with barettin have proven their potential. Also surface topology mimicking the skin of a shark has been shown to be effective.

54.4.2 Biomimetic Adhesives

Today plenty of commercial adhesive agents are biomimetic. The most prominent representative is the gecko tape. The production of such kinds of adhesives is

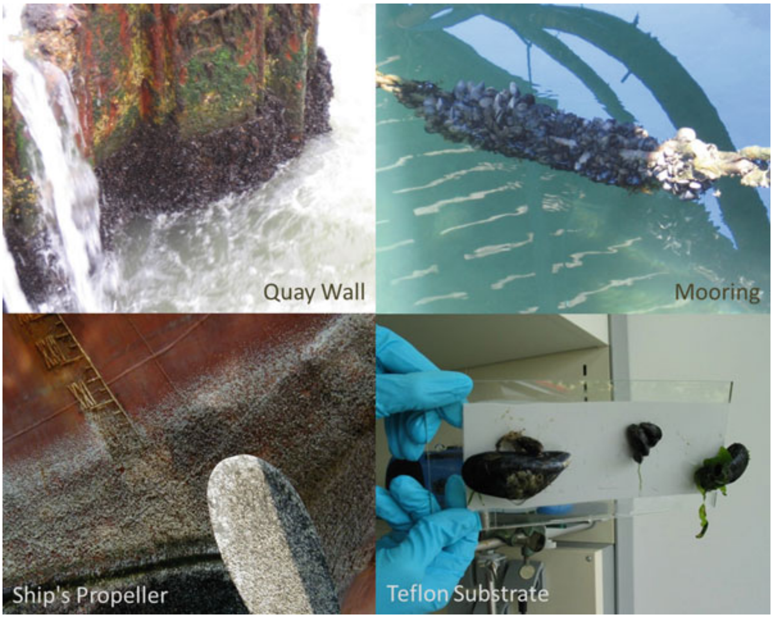

Fig. 3 Macrofouling caused by tough adherent organism, e.g., mussels and barnacles on different surfaces under harsh conditions (salinity, marine current)

estimated to account for 25 billion m^2 (Schwotzer et al. 2012). But for medical issues the market is attractive as well, as the modern surgery is affected by two major factors: cost containment and an aging population (Spotnitz and Burks 2008). Stopping bleedings or sealing and reconnecting tissues after surgical procedures are challenging subjects. The bonding technology emerged as a convenient alternative for wound closure instead of sutures and other tissue applications (Annabi et al. 2015). Recently the slime of slugs (genus *Arion*) was successfully used as an adhesive and sealant for a porcine heart (Li et al. 2017). Many biomimetic tissue adhesives are based on secretions from marine organism, e.g., mussels and algae, but also from terrestrial organism like snails and frogs. Their performance in aquatic conditions is acceptable but requires polymeric additives to adjust the three-dimensional network.

These glues received much attention during the last few years and ended up in mimetics of natural structures like DOPA-containing co-polypeptides and DOPA-functionalized poloxamers or catechol-modified alginate hydrogels (Lee et al. 2013; Bochynska et al. 2016). Red and brown algae also use a mechanism based upon phenolic compounds. Under hydrated conditions their secretions are able to adhere to hydrophilic as well as hydrophobic surfaces. An enzyme (vanadate-peroxidase) induces the cross-link between the polyphenol and the extracellular carbohydrate fibers and causes adhesion to the surface. Hence carbohydrate-based adhesives are worth imitating. Thus, an alginate-polyphenol hybrid adhesive, mimicking *Fucus serratus*, showed higher adhesion to Teflon™ than to glass (Kumar Patel et al. 2013).

As promising candidate the Australian frog *Notaden* was also identified as it exhibited five times stronger adhesive strength than fibrin glue on sheep meniscus tissue (Graham et al. 2005).

Various types of medical adhesives are in use as hemostats to form a barrier and stop bleeding (protein and polysaccharide based) or as sealants in order to establish an impervious barrier to gas and many body liquids (fibrin sealant, polyethylene glycol, albumin, and glutaraldehyde) or as adhesives to connect tissue or medical devices (cyanoacrylates, albumin, glutaraldehyde, and fibrin sealant) (Spotnitz and Burks 2008; Ferguson et al. 2010). This classification refers to their function in surgical context. With respect to the former sections, a division could also be used to summarize the medical adhesives according to the compounds' origins:

(i) Natural or biological adhesives (protein based, sprayable foams or dry fibrin sealants, collagen, gelatine; polysaccharide based, chitosan, alginates, dextran, chondroitin sulfate glue)
(ii) Synthetic and semisynthetic adhesives (albumin and glutaraldehyde, cyanoacrylates, polyurethanes, polyvinyl alcohol, polyethylene glycols, dendrimers)
(iii) Biomimetic adhesives (mussel, sandcastle worm, frog, slug)

The development of high-performance adhesives for use with living tissue as shown in Fig. 4 keeps the surgical toolbox expanding (Spotnitz and Burks 2008). More insight is given in ▶ Chap. 58, "Adhesion in Medicine."

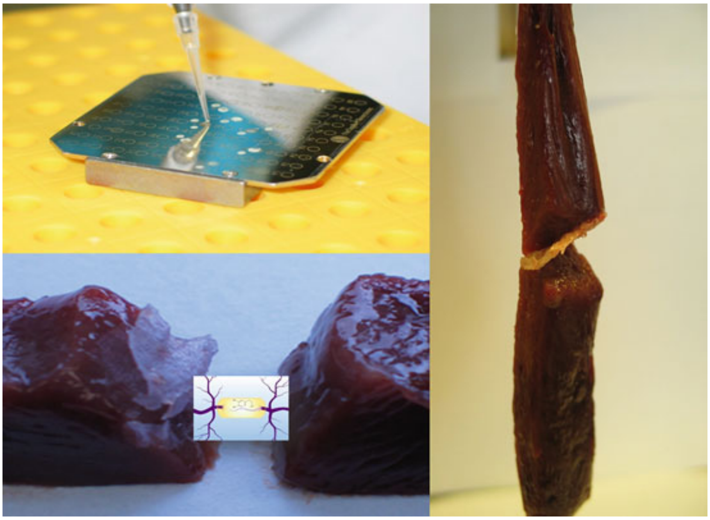

Fig. 4 Investigation and characterization of biological adhesives by MALDI-TOF MS, application of a biomimetic adhesive to soft tissue and testing the joints (Images from Ingo Grunwald, Fraunhofer Institute for Manufacturing Technology and Advanced Materials (IFAM), Bremen, Germany, and reproduced with his permission)

54.5 Challenges and Opportunities

Each of the reviewed bioadhesives has advantages and drawbacks. In terms of *bacterial adhesion*, approaches for a forensic usage are in discussion. Considering that everyone's microbiome is highly individual like DNA is, the microbial fingerprint is a valuable hint in criminal investigations. But depending on the kind of test and recognition of the microbiome, this approach can be risky: in case of sequencing the genetic material, the latter can be manipulated by malicious software encoded into the physical nucleic acid strand. The resulting data can corrupt gene-sequencing software and take control of the underlying computer-aided analysis (https://www.wired.com/story/malware-dna-hack/). Adhesion at this minor scale in crime context as well as with regard to antifouling efforts reveals its high potential. So does the use of some algae and their adhesion to surfaces triggered by certain wavelengths of the light. Based on such knowledge, adhesion could be prevented by manipulations involving intelligent materials, for instance, modified materials in bioreactors.

Referring to carbohydrates chitosan displays impressive potential as fully bio-based adhesive (5 MPa shear strength on pine wood) (Kumar Patel et al. 2013). Microbial polysaccharides blended with surfactants showed trendsetting results as well. However, as with sugars, there is an increasing tendency to abandon starch solutions in choosing binders for clay and pigments. Preferable would be combinations of synthetic latexes with casein or vegetable proteins instead of starch dispersions.

Coming to proteins, many investigations in terms of constructional applications have indicated potential: gluten as a substituent (25%) in phenol-formaldehyde resin masses for use in particleboard production (medium-density fiberboard, MDF) did not affect the mechanical performance. As gluten is a by-product from the glucose syrup production, the costs (about 300 euros/t referred to protein desiccant) are more than one sixth less than urea-formaldehyde resins (363 euros/t) (Türk 2014). Assuming that the cost of such binders contributes about 25% to the production costs, a substitution might be more economic, even if more process time is required. Native proteins are mostly insoluble due to their tertiary or quaternary structures. Processing like degradation or reduction can impart the solubility for its use in adhesive formulations. In general proteinaceous adhesives combine biodegradability more favorably and are much more water resistant compared with carbohydrate-based adhesives. Except for chitosan "bio-based" mostly have a positive impact to any life cycle assessment as a substitute to petrochemical compounds, and they show just a few or no emissions.

Complete substitution of synthetic components to compete with commercial adhesives still needs to be realized. Intermediate bio-based adhesives are therefore just a compromise.

The construction and building sector remains as one of the most significant markets for adhesives. Their uses of adhesives range from flooring to structural purposes or building envelopes.

The family of medical adhesives represents another relevant market. Although "classical" medical adhesives and those specific for medical as well as dental devices are rather heterogeneous, they can be grouped into one family. The global market for medical adhesives and sealants is estimated to reach over 15 billion US dollars in the year 2022 (http://www.strategyr.com/MarketResearch/Medical_Adhesives_and_Sealants_Market_Trends.asp). Driven by an aging population, increasing surgical operational interventions, the rise in healthcare needs, and new treatment methods like the preferences for minimal invasive methods or the use of new tissue scaffold applications, the CAGR (compound annual growth rate) in the area of medical adhesives will reach top values of about 10% until 2021, with even higher values expected for the Asia-Pacific area (http://www.strategyr.com/MarketResearch/Medical_Adhesives_and_Sealants_Market_Trends.asp).

The consciousness of the benefits involved by using bioadhesives in multiple areas (e.g., health, environmental, ethical) is evolving. Bioadhesives are popular; six billion US dollars have been estimated for the global market in 2019. It is possible to increase the sustainability of industrial processes while maintaining or increasing the competitiveness of enterprises. As long as the legislatures are aware of the need to go ahead with the development of bioadhesives and the technologies of second-generation biofuels, the development of bioadhesives will lead to products that can cope with commercial adhesives. Last but not least, the requirements for reducing the emissions of volatile organic compounds (VOCs) and the requirement for recyclable materials push the development of bioadhesives (Mathias et al. 2016).

The classical medical adhesives are normally grouped into (depending on the classification system) hemostats which stop bleedings, sealants which seal leakages (gas and nonclotting liquids), or adhesives that “glue” two tissues together.

This segment of classical medical adhesives alone will have a market size of about three billion US dollars in 2021 (markets) – indicating a highly attractive field of application for medtech companies today and in the future. The market is dominated by the USA and Europe, but emerging markets like those of South America and Asia offer quite significant growth opportunities. The growth rate is observed and checked, for instance, by the process of regulatory affairs (the USA with the FDA, Europe with CE marking) for the certification of new medical adhesives. At least in the EU, the process of the approval of medical devices like adhesives will be tightened due to new regulations. Regardless of this situation, the medical adhesive market and the research associated with it are expected to have a bright future.

54.6 Conclusion

Biological and microbiological adhesives have an enormous potential for industrial applications. The most prominent ones are constructional, packaging, and medical applications. Sustainable packaging will prevail. There is, however, also a need for manipulating and adapting biological adhesion for healthcare or food safety issues. On account of their impressively efficient and precise way to adhere to industrially challenging substrates, these materials need to be studied and the conditions under which initial adhesion occurs want to be understood. Thus, any activity furthering insights into the principles of these compounds is significant, reflecting, for instance, the current worth of the stem cell industry 3.5 million pounds in the UK alone (Waugh et al. 2016).

Developing biocompatible adhesives with strong adhesive properties for medical applications is highly desirable, but the delicate balance between adhesive performance and biocompatibility is crucial and part of the legal and technical requirements. Although “tissue adhesives are far from ideal” (Li et al. 2017), there are many promising approaches under investigation (Balcioglu et al. 2016; Li et al. 2017).

Nearly all of the reviewed adhesive classes are important subjects of research to develop alternatives for petroleum-based materials, and the quest exists to develop bioinspired solutions and to achieve tailored adhesives for specific tasks including the prevention of fouling. As carbohydrates and vegetable proteins can be obtained from waste streams of renewable resources and may be produced in great abundance, they do not have to compete with food production and can be considered as a sustainable option. Nature is a prime candidate for inspiration and provides raw materials for applications in adhesives. Bioadhesives can be converted into a variety of useful adhesive products with a promising future, even if natural variations in quality are weaknesses. The interdisciplinary approach with inputs from chemistry, physics, bionics, biology, and engineering offers a wide range of possibilities. Thus, outstanding adhesive performance in nature can be elucidated on a molecular level and translated into technical concepts. Mechanical discrepancies can be bridged with hybrid materials from biological concepts in combination with synthetic components. Looking just at the largest market for adhesives (construction), a fast-growing market (packaging), and the exclusive market (medical adhesives), the future prospects for bioadhesives are positive. This trend is clearly evidenced by the increase in relevant publications covering the field over the last few years (Babu et al. 2013).

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