Introduction

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One contribution of 15 to a theme issue
‘Biological adhesives: from biology to biomimetics’.

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Biological adhesives offer impressive performances and, therewith, the potential to inspire novel, more reliable, efficient and environmentally friendly adhesives for an increasing variety of applications. Adhesives found in nature do indeed perform in ways that man-made products simply cannot match. Some are reversible, others work most effectively underwater and many are universal in their performance to substrates of varying composition and structure. No wonder then that of all biological phenomena that have been investigated with a biomimetic purpose, bioadhesion has perhaps received the most interest. However, our knowledge of natural adhesive systems remains distant from the engineering of innovative adhesives for specific industrial needs. It is necessary therefore to understand the mode of action of biological adhesives and to elucidate their basic components, building principles and function-specific adaptations selected by evolution. It is this challenge that has been at the origin of the creation of a network of researchers under the auspices of COST, the European Cooperation in Science and Technology. This so-called COST Action ran from 2010 to 2014, and its main objective was the identification of potentially interesting biological adhesives and their functional characterization, so as to facilitate the development of synthetic counterparts with improved function. The series of papers presented in this theme issue stem from the collaborative works conducted within the framework of this COST Action.

Bioadhesion research is a field at the border between biology, biophysics, chemistry and materials science, and the complete characterization of a biological adhesive requires a broad range of techniques and expertise, which are rarely gathered in a single laboratory. In this context, the organization of scientific meetings, training schools and short-term scientific missions in the framework of the COST Action acted as a catalyst to pool knowledge, methods and techniques together, as well as to enable intellectual and practical exchanges. Arguably, the most beneficial contribution of the network was the access it provided for researchers to experimental techniques that they would not otherwise have had the opportunity to use. Through interdisciplinary collaborations, a more comprehensive understanding of bioadhesives has been achieved and ideas for their practical development will be forthcoming.

Nature offers a vast repository of inspiration in the form of organisms using natural adhesives for a variety of functions, including: (i) temporary attachment of body parts together; (ii) attachment of one organism to another (copulation, phoresy or parasitism, prey capture) or (iii) attachment of an organism to a non-living surface, including dynamic attachment during locomotion and permanent fixation. Moreover, environmental constraints can influence the specific design of adhesion mechanisms. For example, terrestrial animals that climb on plants, rocks or other types of unpredictable substrates have evolved structured adhesive organs on their feet, whereas in the aquatic environment, attachment devices developed by animals rely on highly viscous or solid adhesive secretions usually containing specialized adhesive proteins. Such glues can also be used by some terrestrial organisms. The diversity of biological attachment devices is therefore huge. Yet, only a very limited number of model systems have inspired most biomimetic approaches, including the well-known gecko foot for dry adhesion and mussel glue for underwater adhesion. To
circumvent this bottleneck, most of the studies gathered in this theme issue relied on a bottom-up approach in which new biological models of adhesion, from both terrestrial (e.g. geckos, frogs, insects, spiders and plants) and aquatic (e.g. barnacles, octopuses, sea squirts and algae) habitats were characterized. Their aims were: (i) to isolate adhesive molecules and characterize them at both the biochemical and/or physico-chemical levels, (ii) to analyse the complex micro- and nano-scale hierarchical structures of bioadhesives, (iii) to quantify the adhesive and frictional performance of bioadhesives, as well as their material properties and tribological interactions under standardized conditions, and; (iv) to develop models helping to identify the key principles of biological adhesives that would be useful for the design of synthesized adhesive systems.

The physico-chemical characterization of biological adhesives is very challenging since usually the amounts produced are quite low and the adhesives usually consist of complex blends of different biopolymers. Hennebert et al. [1] reviewed the experimental strategies that have been successfully used to identify, characterize and obtain the full-length sequences of adhesive proteins from nine biological models: echinoderms, barnacles, tubeworms, mussels, sticklebacks, slugs, velvet worms, spiders and ticks. Their survey concludes that the dual proteomic and transcriptomic approach is currently the best way to identify novel adhesive proteins and retrieve their complete sequences. The list of adhesive protein sequences deposited in public databases has thus increased tremendously in recent years. However, there are still many organisms for which little is known about the adhesive strategies and molecular mechanisms. This is the case for ascidians, as reviewed by Rothbächer & Pennati [2] who summarize the current knowledge on the adhesive mechanisms of their larvae and discuss the potential of developmental and functional genomics to advance our understanding of cellular and molecular adhesive signatures. Contrary to ascidians, barnacles have been widely studied but, despite years of dedicated research, it is still not clear which molecular mechanisms allow them to permanently adhere to surfaces underwater. Jonker et al. [3] used elemental analysis and various spectroscopic techniques to investigate the adhesion of the stalked barnacle Lepus nutitien. Their results highlight some differences in the chemistry of their adhesive compared to those of acorn barnacles that have dominated previous research. In barnacle larvae, one protein, SIPC (settlement-inducing protein complex), is present in the larval temporary adhesive secretion and, therefore, plays a double role in settlement and adhesion. Petrone et al. [4] report on the measurement of the adsorption behaviour of SIPC to various surfaces. The establishment of the bond for biological adhesives does indeed start with the adsorption of the adhesive biopolymers to the surface. Using surface plasmon resonance, they show that SIPC can adsorb irreversibly and non-cooperatively on a series of self-assembled monolayers at the pH of seawater. Interfacial effects are predominant in adhesion and surface modifications may either promote or deter bonding. Ritimi et al. [5] demonstrated that polymer surface pre-treatment enhances the adhesion of titanium oxide which, in turn, interacts with the cell wall of bacteria, leading to their inactivation.

Biological adhesives usually possess complex hierarchical structures from the micrometric to the nanometric scale, and this structural organization is as important for the function of the adhesive as its chemical composition. Drotlef et al. [6] describe the morphology of the toe pad epithelium of the rock frog, *Staurois parus*, using a variety of microscopy techniques. Cells of this epithelium are covered by a dense array of nanopillars, which may be a specific adaptation for underwater adhesion and friction. Another adaptation to the torrent habitat in which the frog lives is the presence of straight fluid-filled channels crossing the toe pad surface and assisting in the drainage of excess water. These different adaptations are discussed in the perspective of the development of new biomimetically inspired reversible adhesives. Another attachment mechanism that has attracted the interest of scientists in recent years is the octopus sucker. Indeed, the ability of these structures to attach to almost any object or surface is still poorly understood. Tramacere et al. [7] present new anatomical and histological findings on the suckers from several octopus species. The presence of a protuberance in the acetabular roof in all the investigated species is pointed out as a key element for performing a smart and energy-efficient attachment. From a technological perspective, the identification of the underlying mechanisms involved in sucker attachment can favour the development of new generations of artificial devices and materials.

For a complete description of biological adhesive systems, information about the chemistry and structure of adhesives must be combined with data on their mechanical performance. Of the techniques used to measure the adhesive and frictional performance of adhesives, as well as their material properties, many are well established in the field but others have to be developed specifically. It is the case of the novel flow channel presented by Dimartino et al. [8]. This channel makes it possible to test the adhesion strength of the microscopic germlings of the macroalga Hormosira banksii on various substrates. In this model, adhesion strength does not vary according to substrate but increases in a time-dependent manner on all surfaces. In addition, computational fluid dynamics indicate that, on average, the drag force decreases with increasing germling number, suggesting that germlings would benefit from gregarious settlement. Another example of a water-resistant adhesive is the one secreted by the stalked barnacle Dosima fascicularis. Zheden et al. [9,10] studied this species because its foam-like cement is produced in larger amounts than the cement of other barnacles, and because it plays a dual role, providing attachment but also buoyancy to the animal. The cement of *D. fascicularis* is soft and visco-elastic, possessing values of elastic modulus, hardness and tensile strength that are considerably lower than in the rigid cement of other barnacles. It also contains numerous large gas-filled cells, the gas volume being on average 18.5%. Moving from under water to wet environments, adhesion measurements are also reported for the carnivorous plant *Roridula gorgonias*, which releases a viscous resinous secretion by glandular trichomes. Voigt et al. [11] demonstrate that even after being submersed for 24 h in water, the trichomes maintain their ability to adhere to both hydrophilic and hydrophobic glass surfaces, a fact that is attributed to the presence of acyl glycerides and triterpenoids in their secretion. The robustness of the secretion to a wet environment presumably enables the plant to maintain its trapping function also under humid conditions and during rainy weather. Among terrestrial organisms, insects are one of the species-richest group comprising numerous successfully evolved models relying on biological adhesion. In the green dock leaf beetles *Gastrophyse viridula*, Zurek et al. [12] measured attachment ability of larval instars.
by centrifugation on a spinning drum. This beetle larva uses pretarsal adhesive pads on thoracic legs and a retractable pygopod to attach to and walk on smooth surfaces and ceilings. Both adhesive organs are soft smooth structures and capable of wet adhesion. The respective contribution of each adhesive organ to total attachment ability, investigated by selective disabling, indicates that, despite their smaller overall contact area, tarsal pads contribute to a larger extent to total attachment ability, likely because of their distributed spacing.

Experimental data on biological adhesives can be integrated into theoretical models of adhesion and friction. Such models help in identifying key principles where natural systems show a better performance. For example, one of the important problems appearing in experimental realizations of artificial fibrillar adhesives inspired by gecko foot hair is the so-called clusterization. Artificially produced structures have to be flexible enough to allow efficient contact with natural rough surfaces, but after a few attachment/detachment cycles, the fibres of the structure tend to adhere to one another and form clusters that form much worse adhesive contacts than the original fibres. To address this issue, Filippov & Gorb [13] use a numerical simulation of the three-dimensional spatial geometry of non-uniformly distributed branches of nanofibres, investigate the attachment–detachment dynamics and discuss its advantages over uniformly distributed geometry. Another problem of artificial adhesives is delamination. Brély et al. [14] develop a novel numerical model to simulate the multiple peeling of structures with arbitrary branching and adhesion angles, including complex architectures. The predictions of this model are in excellent agreement with the recently developed multiple peeling theory that extends the energy-based single peeling theory of Kendall. The model is also applied to study spider web anchorages, showing how their function is achieved through optimal geometrical configurations.

Endnote