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ScienceDirect
Acta Biomaterialia 5 (2009) 1848–1854
Acta BIOMATERIALIA
www.elsevier.com/locate/actabiomat

Biomimetic replicas: Transfer of complex architectures with different optical properties from plant surfaces onto technical materials

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Received 5 August 2008; received in revised form 15 January 2009; accepted 16 January 2009
Available online 31 January 2009

Abstract

Plant surfaces are characterized by a high diversity of structures which determine their optical properties, such as shiny, gleaming, silky, matt or iridescent. Replicas with different optical properties have been generated by using plant surfaces as templates and an improved replica technique. The technique allows the replication of complex surface structures with overhangs, cavities, and fragile or soft structures in a fast and cost-efficient way. Structures from some millimetres to some nanometres can be replicated. The transfer of complex architectures with different optical properties from plant surfaces onto technical surfaces implies a great potential for the development of new biomimetic surfaces with new optical properties.

Keywords: Moulding; Replica technique; Optical structures; Soft lithography; Biomimetic surfaces

1. Introduction

Many biological surfaces possess a hierarchical topography built up of a combination of micro- and superimposed nanostructures. Within plants, microstructures are usually formed by convex cell sculpturing or by multicellular structures [1]. Nanostructures on plant surfaces are usually formed by epicuticular waxes and cuticular folding [2]. The surface structure influences the optical and physical properties of the surfaces, such as their wettability or spectral properties for light reflection [1]. Different combinations of such structures cause different grades of reflectivity, for example the papillae cells of many flower leaves (petals) intensify the colouration [3]. Hairy trichomes, formed by surface cells, can significantly increase the reflection of light [4].

Biological surface structures and their properties can be used as models for biomimetic materials, such as superhydrophobic and self-cleaning surfaces [5,6]. The topography of the shark skin was successfully transferred onto artificial materials to reduce drag during movement under water or in air [7]. Therefore, development of hierarchical micro- and nanostructured biomimetic surfaces is of great economic and scientific interest. Furthermore the degree of reflectivity and optical appearance of technical surfaces are important properties for a wide variety of materials, such as paper, paintings and polymers [8].

However, existing techniques for surface micro- and nano-structuring are often related to expensive and extensive techniques such as wet and dry etching, electron and ion beam lithography, electrochemical deposition, plasma spraying, micromachining and physical vapour deposition techniques [9,10]. In contrast, soft lithography is a common technique to reproduce the structures of a master surface and with this simple, low-cost and fast surface replication technique, structures with a precision of a few tens of nanometres can be generated [9,11]. However, this technique often requires vacuum conditions or strong mechanical pressure to ensure that the moulding materials infiltrate all spaces between the surface structures. These conditions

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doi:10.1016/j.actbio.2009.01.028

limit the application of this technique to mechanically stable, dry biological samples or artificial structures.

Existing moulding techniques for the replication of plant surface structures such as cell papillae and cuticular folding were used by Wagner et al. [12] and Fürstner et al. [13]. Several attempts have been made to mould hierarchical plant surface structures, such as the cell papillae of lotus leaves and their waxes [14–16]. In these techniques the biological material was exposed to vacuum conditions, which leads to the shrinking of cells by water loss and the typical wax tubules of a lotus leaf could not be replicated. A first successful replication of single wax platelets was possible after moulding the waxes and removing them from the mould by chloroform washing (lost wax or *cire perdue* process) [17]. With this technique, fragile three-dimensional wax sculptures with high aspect ratios were replicated. Koch et al. [18] investigated the precision of different moulding materials and selected a material combination of the dental polymer President light body® (PLB) and epoxy resin to minimize the aberration between the sizes of the biological template and the replicas. With these materials and by using a soft moulding technique, plant surfaces with wax crystals on them could be replicated without inducing shrinking artefacts of the cells under ambient conditions. The precision of the technique was verified by the replication of single wax crystals and their characteristic molecular steps of approximately 4 nm height [18].

Here, the moulding technique introduced by Koch et al. [17] was improved for replication of three-dimensional surface structures with overhangs, e.g., hairy plant surfaces. We also selected a wide variety of optical different plant surfaces to transfer their structures and optical appearance onto the moulding material. Reflectometric measurements were performed to quantify the optical properties of the biomimetic replicas.

2. Material and methods

2.1. Plants

Upper leaf/petal sides (adaxial) of 12 species, cultivated in the Botanic Gardens of the University of Bonn (BG Bonn) Germany, were used: leaves from *Caladium bicolor* (BG BONN 24750), *Calathea zebrina* (BG BONN 01201), *Maranta leuconeura* (BG BONN 05028), *Musa uranoscopus* (BG BONN 03502), *Fittonia verschaffeltii* (BG BONN 11142), *Ficus elastica* (BG BONN), *Kalanchoe tomentosa* (BG BONN 05152), *Salvinia biloba* (BG BONN 14459), *Salvinia cucullata* (BG BONN 18268); petals (flower leaves) from *Chrysanthemum leucanthemum* (BG BONN 23433), *Tulipa gesneriana* (BG BONN 105306) and *Viola x wittrockiana* (BG BONN). Species without accession numbers were only temporary cultivated in the Botanic Gardens of the University of Bonn. Nine of the species possess surfaces which differ in their optical appearance and three differ in the type of hairs on their surfaces.

2.2. Material for replication

For generation of negative moulds President light body® (polyvinylsiloxane (PVS), ISO 4823, Coltene Whaledent, Hamburg, Germany) was used. As filler for the generation of positive moulds an epoxy resin (Epoxydharz L®, Nr. 236349; Conrad electronic, Hirschau, Germany) with hardener (Härter S, Nr. 236365, Conrad electronic, Hirschau, Germany) was used. The mixing ratio of epoxy resin and hardener was 10:4.

2.3. Replication process

The moulding technique used here follows the two-step replication process, introduced by Koch et al. [18]. Here, we briefly introduce the technique and highlight the changes made compared to Koch et al. [18]. First a negative stamp of the biological master surface was prepared. In this step the pre-polymer (PLB) is automatically mixed by using a dispenser (PRESIDENT Plus Jet™ light body 48 ml, coltène whaledent®, Altstätten, Switzerland). The PLB was applied onto the biological master surface and immediately pressed down gently using an object slide or a petri dish. After hardening (approximately 2 min at room temperature) the negative mould was peeled off the master surface. For hairy and waxy surfaces the biological master surface can be used only once, because waxes embedded into the moulding material are removed from the plant surface [17] and very long hairs, such as those of *Kalanchoe tomentosa*, can be damaged during peeling off. However, surfaces with cuticle folding and even hair papilla cells can be moulded several times, as long as the biological material does not shrink after water loss. Two hours later, after relaxation of the polyvinyl material, the mixed epoxy resin with the hardener was applied onto the negative mould. In the case of surface structures with a high aspect ratio, air can be captured between the structures and the moulding material. Thus specimens were placed into a vacuum chamber at 1 mbar for approximately 1 min to remove the air between the surface structures. The specimens were then dried at room temperature for 24 h and the replicas were peeled off the positive mould. The second step of replication has been repeated up to 10 times, using the same negative mould, and all replicas were of the same high quality. Subsequently, the replicas were sputter-coated with a 30 nm gold layer (Balzers Union SCD 040, Balzers-Pfeifer GmbH, Aßlar).

2.4. Scanning electron microscopy (SEM)

Fresh plant material was dehydrated with ethanol and dried in a critical point dryer (CPD 020, Balzers Union, Liechtenstein). For analysis of wax structures samples were prepared by using the glycerine-substitution method [19]. Prior to SEM observation all samples were sputter-coated with a 30 nm gold layer (Balzers Union SCD 040, Balzers–Pfeifer GmbH, Aßlar). SEM images were recorded

ID	Title	Pages
1241	Biomimetic replicas: Transfer of complex architectures with different optical properties from plant surfaces onto technical materials	7