NATURAL HIERARCHICAL STRUCTURES AND THEIR REPLICATION

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Abstract

Hierarchical plant surface structures show many characteristics that are an inspiration for humans. They are associated with the process of photosynthesis and provide a hydrophobic or a hydrophilic behaviour, an absorption of solar radiation, etc. Due to evaluation of synthetic analogical structures we are able to obtain important information about their potential applicability in a technical practice. The easiest way to prepare them is a two-stage replication process. This process involves the creation of the so-called first replica, that is the mould for the second replica - the "copy" of natural surface. Replicas can be made from various types of polymers. The aim of the paper is to compare the influence of different types of polymers on the character and quality of synthetic structures - replicas. A hierarchical structure of the pansy flower *(Viola x wittrockiana)* was selected as a replication pattern. The silicone elastomer President Light Body (Coltene Wahledent, Hamburg, Germany) was used for the first (negative) replicas preparation. Thermoset (EP), thermoplastic (HDPE), biodegradable polymers (PCL, PLA), as well as aqueous (PVA) and alcoholic polymer solutions (PVB) were used to create the second (positive) replicas. Replicas quality was evaluated by scanning electron microscopy (Carl Zeiss ULTRA Plus) and by contact angle measuring (See System E). Different hierarchical surface structures and different contact angles were identified according to types of polymers (amorphous, semi-crystalline, chemical composition) and used technology of replication. Easy, fast and a low cost replication process can be used for copying structures up to hundreds/tens of nanometers.

Keywords: Nanostructures, biomimetics, hierarchical plant surfaces, replication, polymers

1. INTRODUCTION

The surfaces of natural objects show a number of interesting properties related to their structure and chemical composition. Hierarchical structures of plant/petal surfaces are very often built up by conically shaped epidermal cells at micrometre levels. Their surfaces are covered with nanostructured wax shapes in form of platelets, tubes or rods. The surfaces structured by the plant provide a protection against excessive wetting and excessive sunlight. They can act as sensors or light-catching systems, too [1,2]. Preparation of synthetic structures and their further testing is interesting from the technical practice point of view. At present, a number of experiments are being carried out to use of natural models. For example, these experiments are: increasing photovoltaic panels performance (pansy and rose petal surface), testing of self-cleaning surfaces (the lotus leaf surface) and a study of antibacterial surfaces based on physical behaviour (cicada and dragonfly wings) [3,4]. Preparation of synthetic structures for the selected properties testing is complicated due to their structural and dimensional hierarchy - nanometre structures are located on larger ones. A selection of the proper material for replica production as well as a low cost technological process is important. Laser, etching and even 3D printing are not suitable processes for the preparation of copies of the natural surface because it is not possible to copy the natural pattern in all its details. The two-step process of replication is an effective, fast and inexpensive way to prepare synthetic hierarchical surface samples. A silicone elastomer is used for the preparation of the mould (so-called the negative/the first replica), whereas an epoxy resin or a silicone elastomer is the most commonly used polymers for the preparation of synthetic samples (so-called the positive/the second replica) [2,3,5]. An evaluation of the influence of different polymers characteristics and quality of synthetic replicas is the aim of this article.

2. EXPERIMENTAL PART

A two-step replication process was used for the preparation of the petal surface polymer replicas. This process is called a soft lithography. Replica analysis was based on the evaluation of scanning electron microscopy micrographs and evaluation of contact angles of synthetic structures from different polymers

2.1. Materials

A pansy *(Viola x wittrockiana)* petal epidermal structure was selected for an evaluation of the replication process, the influence of polymer type on quality and properties of prepared replicas. The pansy petal surface is a typical hierarchical structure of epidermal cells at micrometre and sub-micrometre levels. The elastomeric material President Light Body (Coltene Wahledent, Hamburg) was selected for the preparation of moulds. Materials for the polymeric sample preparation were: epoxy resin EnviPOXY®, (Spolchemie, a. s.), high density polyethylene HDPE (Goodfellow GmbH), polylactic acid PLA (Goodfellow GmbH), polycaprolactone PCL (Merck KGaA), polyvinyl alcohol PVA (Merck KGaA) and polyvinyl butyral PVB (Merck KGaA). The selection includes thermosetting polymer, thermoplastics, biodegradable polymers, water and alcohol soluble polymers, amorphous and semi-crystalline polymers.

2.2. Technology of replication

Fresh and clean pansy petals were used for a surface structure replication. A sample was glued to a flat surface, was covered with a silicone elastomer and was loaded with a force up to 5 N. The crosslinking time of the silicone elastomer was 3 minutes at normal laboratory temperature. Thereafter the elastomer layer was removed from the plant surface, thereby creating the mould. This first replica was consequently and repeatedly used for the preparation of positive/the second replica from different type of polymers. A clean, dry mould was used for the casting of epoxy resin, PVA and PVB. The crosslinking process of epoxy resin samples runs at normal laboratory temperature during 24 hours, in a special vessel at a pressure of 0.7 MPa. Used epoxy resin filled the microscopic and sub-microscopic structure details of the mould well and minimized non-homogeneity of replicas due to an overpressure process. Evaporation of the solvent (water or alcohol) from PVA, respectively PVB solution took place in the air at normal laboratory temperature without overpressure. Samples of HDPE, PCL, and PLA were prepared by melting the polymer granules and subsequently compressing molten mass in the mould. In order to ensure a desired homogeneity of polymer replicas, namely a good filling of microscopic and sub-microscopic details of a mould, a force of 3 to 6 N was used. Thermoplastic replicas solidified during a few minutes.

The following materials and conditions were used to produce replicas: EnviPOXY®, curing agent Telatit 0492, modified cycloaliphatic amine (100 : 27 wt%), a curing time of 24 hours, a curing temperature of 22 °C, an overpressure of 0.5 to 0.8 MPa. 10 wt% aqueous solution of PVA, an evaporation of the solvent in the air for 12 hours, 10 wt% an alcoholic solution of PVB, an evaporation of the solvent in the air for 12 hours. HDPE granules, a melting temperature 190 °C, a melting time 5 minutes, a loading 3 to 6 N. PLA granules, a melting temperature 180 °C, a melting time 5 minutes, a loading 3 to 6 N. PCL granules, a melting temperature at 70 °C, a melting time 5 minutes, a loading 3 to 6 N.

2.3. Analytical methods

The surface structure of pansy petal as well as all type polymer replicas were investigated by scanning electron microscopy (FE SEM Zeiss ULTRA Plus). All samples were sputter coated with a 4 nm Pt-Pd layer (Quorum Q150R ES) prior to SEM investigation. Additional information was determined by static contact angle measurements (See System E). For this purpose 5 μl droplets of distilled water were applied on the replicas surfaces.

3. RESULTS AND DISCUSSION

The pansy flower conical cells show a diameter approximately 30 to 40 μm at the base, wrinkles on the top of epidermal cells and folding typical for all cultivar of pansy (**Figure 1)**. The thin layer was retrieved from the surface of a flower petal. Due to the minimal volume of water in this layer only a slight deformation of the actual conical structure has occurred. Well visible folds show thickness from 200 to 300 nm. The epidermal cells height is about 40 μm.

Figure 1 The natural petal surface - epidermal conical cells of pansy *(Viola x wittrockiana)*

The silicone elastomer mould (**Figure 2**) is a good copy of the epidermal cell surface sample both at the micrometer and the sub-micrometer size. Foldings in the mould do not appear to be sufficiently deep in the images compar ed to the plant specimen.

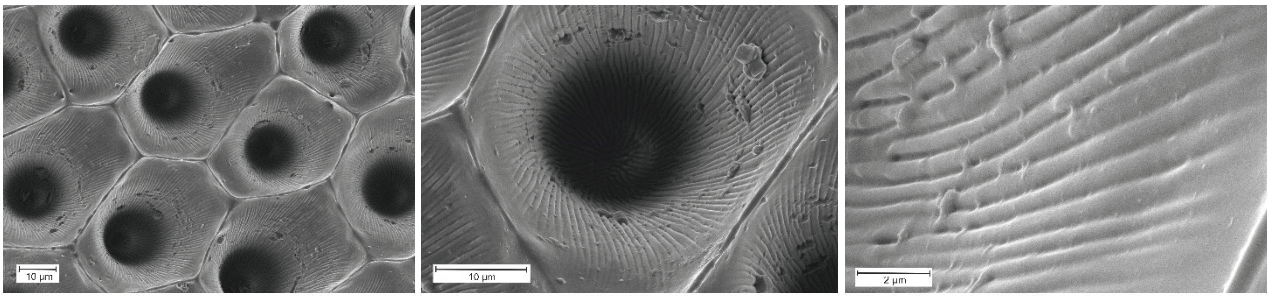

Figure 2 Silicone elastomer mould surface - negative replica

The epoxy resin (**Figure 3**) copies the pansy surface sample very well. Both epidermal cells of dimensions from 30 to 40 μm, as well as 200 to 300 nm folds are well visible.

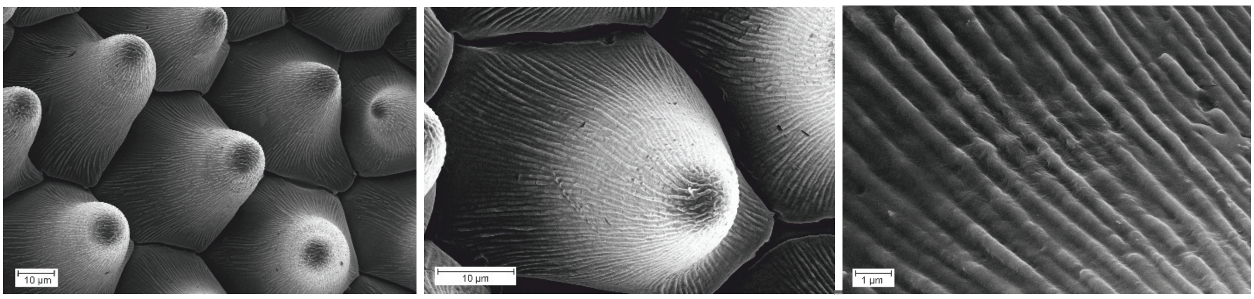

Figure 3 Synthetic replica of the plant surface - epoxy resin (EnviPOXY®)

The polyvinyl alcohol (**Figure 4**) copies the shape, the diametre and the folds of the pansy surface sample. Both epidermal cells of dimensions from 30 to 40 μm, wrinkles on the top of epidermal cells, as well as 200 to 300 nm folds are well visible. The surface of the folds is not smooth.

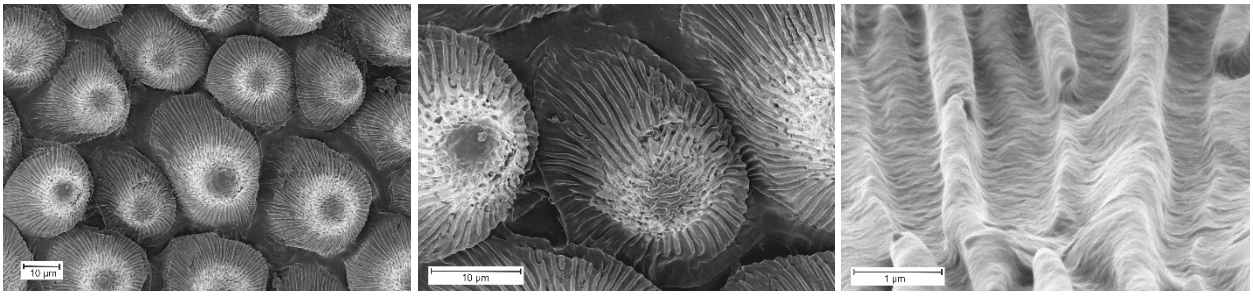

Figure 4 Synthetic replica of the plant surface - polyvinyl alcohol (PVA)

The polyvinyl butyral (**Figure 5**) copies the shape, the diametre and the folds of the pansy surface sample. The epidermal cells and the wrinkles on the top of epidermal cells are well visible. The folds are shallow compared to others polymer replicas. The surface of the folds is not smooth, visible particles were not studied in more detail.

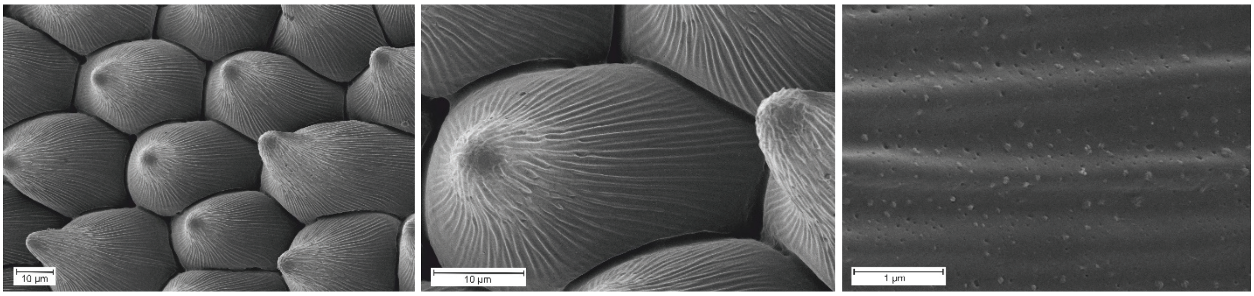

Figure 5 Synthetic replica of the plant surface - polyvinyl butyral (PVB)

The polylactic acid (**Figure 6**) copies the shape and the diametre of pansy surface sample similar as in previous examples. The folds are shallow, the surface of the folds is not smooth but it contains pores and visible particles. These inhomogeneities were not studied in more detail. The polylactic acid is a polymer with a low level of crystallization.

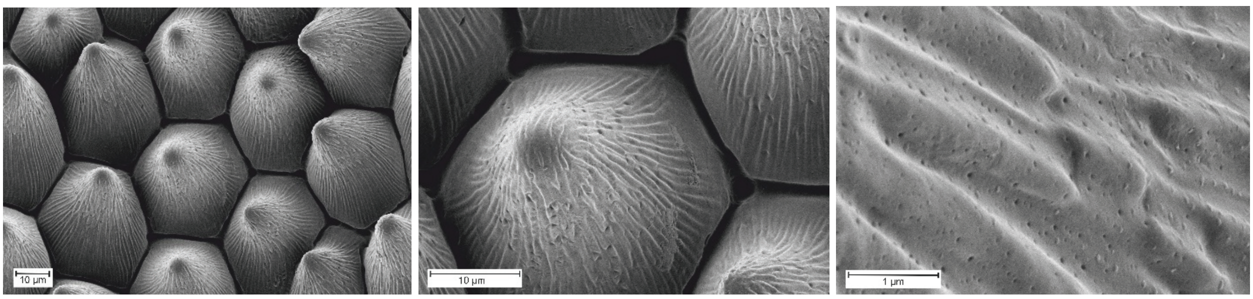

Figure 6 Synthetic replica of the plant surface - polylactic acid (PLA)

The polycaprolactone (**Figure 7**) copies the shape, the diametre, the wrinkles on the top of epidermal cells and the folds of the pansy surface sample. The folds are shallow, inhomogeneous with a slightly fibrous structure compared to other polymer replicas. The depth and dimensions of the folds do not reach the quality of the plant sample. The fibrous surface of the folds was not studied in more detail. The polycaprolactone is a semicrystalline polymer.

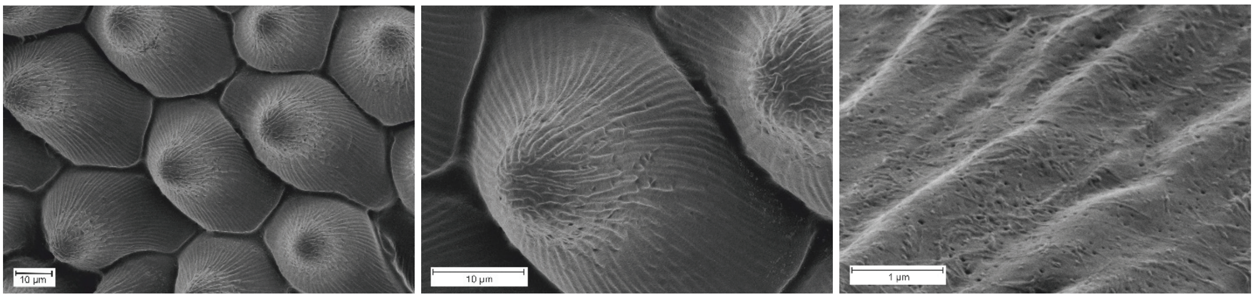

Figure 7 Synthetic replica of the plant surface - polycaprolactone (PCL)

The high density polyethylene (**Figure 8**) copies the shape, the diametre and the folds of the pansy surface sample. Both epidermal cells of dimensions from 30 to 40 μm, wrinkles on the top of epidermal cells, as well as 200-300 nm folds are well visible. The surface of the folds is not smooth but a new fibrous structure was created. The visible fibers are 10 to 20 nm in size and are transversally arranged to the folds. The high density polyethylene is a semicrystalline polymer.

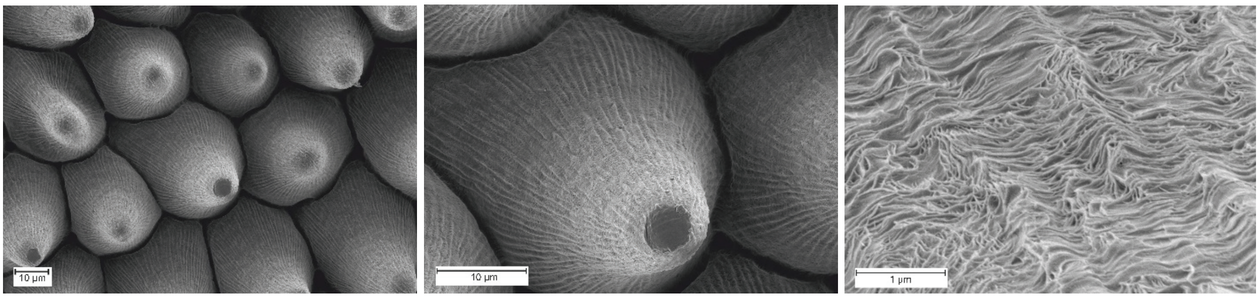

Figure 8 Synthetic replica of the plant surface - polyethylene (HDPE)

From the point of view of the replication process, all replicas prepared from the above mentioned polymers show good compliance with the pansy pattern on the epidermal cells level. The nanostructure built up from the tens of nanometres densely folded fibres was identified in the case of the high density polyethylene. This substructure does not appear on the plant surface or on replicas from the other used polymers. The described substructure was not found on the HDPE control samples which were made by a conventional injection moulding into a standard steel mould. This nanostructure was created due to the influence of the used polymer and the technology of replication.

Table 1 Contact angle of the plant pattern, the flat polymer surfaces and the structured polymer replicas

Polymer	**Contact angle of flat surface (°)**	**Contact angle of replica surface (°)**	**Increase of contact angle (%)**
Plant pattern	-	139.8	-
Epoxy resin	59.4	108.6	54.7
PVA*	-	-	-
PVB	72.6	119.9	60.6
PCL	77.8	113.2	68.7
PLA	74.9	110.3	67.9
HDPE	77.3	138.3	78.9

∗ an impossible to measure due to a dissolution of PVA sample in water

The contact angles were measured on the different polymer replicas. The difference in contact angle values depends on the type of the polymer used and the character of the surface. The flat surface of all the used polymers shows the hydrophilic behaviour because the contact angle is lower than 90°. Due to the structuring of the polymer sample surface, the contact angle increases and the polymer replicas surfaces show the hydrophobic behaviour (the contact angle is higher than 90°). The epoxy resin replica shows the lowest contact angle 108.6. On the contrary the HDPE as a semi-crystalline polymer shows the highest value of the contact angle 138.3 (**Table 1**). The difference in the contact angle values can be explained due to the dissimilar chemical composition of the used materials and the distinct surface structure of the replicas that is particularly due to the fibrous nanostructure that was analysed on the HDPE replicas samples. To confirm the pronounced opinion, further experiments will be required to verify the effect of the chemical composition and the influence of the nanofibrous structure.

4. CONCLUSION

The two step method of replication is a very efficient, fast and inexpensive method for the preparation of the polymer samples of the natural surfaces and their further testing. Due to this method it is possible to capture the actual state of the natural surface. The replicas could be created from amorphous and semi-crystalline polymers. The type of the selected polymer has the underlying effect on the resulting structure and contact angle values. The quality of the replication process is at a high level. The new nanostructure was identified in the case of the high density polyethylene. This nanostructure was created due to the influence of the used polymer and the technology of replication.

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