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研究課題名（和文）花弁の透明化のメカニズムとそのバイオミメティクス

研究課題名（英文）Understanding the Mechanism of Flower Petal Transparency Change and Their Applications for Biomimetics

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交付決定額（研究期間全体）：（直接経費）　2,800,000円

研究成果の概要（和文）：花びらの内部構造は光学顕微鏡および電子顕微鏡によって調査され、強い光散乱によって花びらの白色が気泡によるものであることが判明しました。これらの気泡に液体やゲルを満たすことで、不透明度が変化し、花びらは透明になりました。生体模倣のアナログとして、乾燥状態と湿潤状態で同様の透明度変化を示すフッ素化ポリマーの多孔質フィルムを製造することができました。この場合、変化は可逆的であったのに対し、花びらの場合は不可逆的でした。

研究成果の学術的意義や社会的意義
Biomimetics can produce functional materials by environmentally friendly processes that are energy-saving. The transparency change of films without any external triggers offers new applications in remote areas and can be used for automatic shading of windows or as sensors.

研究成果の概要（英文）：The internal structure of flower petals was investigated by optical and electron micrsocopy and we found that air-filled voids are responsible for the white color of the petals by strong light scattering. We were able to fill these voids with liquids and gels that led to a change in opacity - the petals became transparent. As a biomimetic analogue we were able to produce porous films of a fluorinated polymer that showed the same change in transparency when dry and wet. In this case, the change was reversible, while in the petal case, it was not.

研究分野：Polymer Science

キーワード：biomimetics　flower petals　transparency　films

1. 研究開始当初の背景 Background of the research at the start of the project

Biomimetics is a relatively new research area which includes the collection, observation and catalogization of natural structures, organizations, and processes. The aim is a better understanding of biology and their application for an ecofriendly transformation of processes and structures for a sustainable future.

The attractiveness of biomimetic structures is also that they do not necessarily have a biological function. There also should be some ‘side effects’ that themselves then could be exploited as eco-friendly applications.

Plant surface structures have been discovered, described and biomimetically reproduced in increasing numbers and even commercialized in recent years. Famous examples are superhydrophobic Lotus leaves, glossy surfaces, and non-reflecting coatings.

Most flowers need to attract pollinators, such as insects, and olfactoric and visual clues are most common. Thus, many flowers are visually attractive. But those additional features use resources and energy, so plants with a less ecological footprint for those additional tasks are favored.

2. 研究の目的 Aim of the research

The skeleton flower (Diphylleia grayi), is a native flower to higher altitudes in Hokkaido and other regions, such as Siberia and North America. It has unimpressively small six white petals with a diameter of approx. 1 cm, but that show a very unusual change in appearance: they turn translucent when wet. Here we attempt to clarify the mechanism by observing the cross section and surface morphology of the petals by scanning electron microscope (SEM) in both the dry and wet stages by the nanosuit method, and by 3-D fluorescence microscopy. These results are compared with petals of other plants, such as Japanese Cherry (Prunus serrulata), Japanese Ladybell (Adenophora triphylla var. japonica), ox-eye dasies (Leucanthemum vulgare), and dandelion (Taraxacum officinale).

Since D. grayi only blooms for a very short period in early spring, we studied to prolong the blooming or shift the blooming period to other months by growing the plant from its rhizome in a climate chamber.

Furthermore, we developed a method to biomimetically reproduce the petal structure in an artificial thin film of poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP). The filsm prepared at various conditions show similar behavior, turning transparent when in contact with water and then back to white when dried.

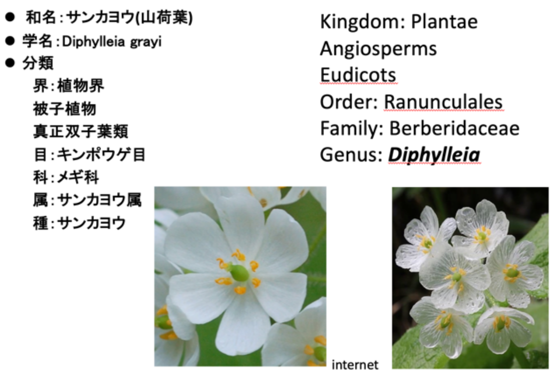

Figure 1: D. grayi description

3. 研究の方法 Experimental

For the studies of wet samples, fresh flowers or their petals were soaked in a polysorbate non-ionic surfactant (Tween 20) (MP Biomedicals LLC, USA) solution. Flower petals were carefully plucked with tweezers at their base and cut with a surgical knife to produce cross section views. For electron microscopy, uncoated petals were imaged in a JEOL JSM-7800F Field emission scanning electron microscopy (FE-SEM). PVDF-HFP films were imaged in a conventional SEM (Keyence VE-8800) or by FE-SEM. For 3-D fluorescence microscopy, fluorescein sodium salt was dissolved in water and added to the tween-20 solution at a concentration sufficiently high for fluorescence imaging (Alpha-3, Opto-Line Inc., Japan).

PVDF-HFP films were prepared by spincoating PVDF-HFP solutions in dimethyl formamide (DMF) on glass slides (Matsunami NEO, size: 1 inch x 3 inch) and dropped into water of various temperatures (40-80° C). The films peeled off the glass slide and floated to the water surface and were transferred onto cellulose paper (Kim Towel) to dry.

Refractive Index was measured with a prism coupler. The reflection of a light beam of dry and wet samples that were attached to a prism was measured and from the angle of total reflection, the refractive index was calculated.

4. 研究成果 Results

4.1. 花弁の特徴 Characteristics of flower petals

The nanosuit® method was first described in 2013 and involves the coating of biological specimen with a thin liquid film of a solution of tween 20, a sorbate-derived amphiphile. In the electron microscope, during irradiation with the electron beam the surface active polysorbate molecules polymerize and form a durable but elastic film that prevents the evaporation of water from the specimen. Thus biological specimen can be imaged in a state that is very close to their natural appearance, and the characteristics of surface nanostructures is not distorted by water evaporation in the high vacuum environment in the electron microscope.

The FE-SEM images shown in Figure 2 were taken at an incident angle of 45° . A fresh (white) petal, a tween 20 soaked (transparent) petal, and a petal after drying (transparent) are shown. The petal surface in the natural white state is covered with tube-like structures with a length of 100-200 µm and a width of 10-20 µm. Their height is difficult to measure, but is estimated to be 5-10 µm given a more or less circular or oval cross-section. The long axis of the tubes is parallel the long axis of the petal. One can see that the pressure applied by the surgical knife to cut the petal in order to observe the cross section is already high enough to collapse the tubular structures close to the cutting edge. The facts that they are easily compressed and no leakage of a liquid can be observed suggest that they are air-filled. The role of those air-filled tubes might be two-fold. The cross-section of the petals reveal their thinness – just 5 to 10 µm – and thus they might provide mechanical stability, since such air-filled structures are light weight and reduce bending in the direction of their long axis. Two layers of tubular structures, one on top and one at the bottom of the petal, add two more interfaces at which light scattering occurs, thus providing the whiteness a 'normal' petal of 5-10 µm thickness could not produce.

The transparent petal in in Fig. 3 (center) shows no clear difference in surface morphology to the white natural state, but one could argue that the tubular structures look a little bit bloated. Since the petal is transparent, the light scattering interfaces should not exist anymore, and we assume that liquid entered the tubular structures.

The dried up petals after becoming transparent are still transparent, but the SEM picture in Fig 2 (right) shows that the tubular structure has collapsed, most likely due to the capillary force that the drying water exerts on the wall of the tubular structure.

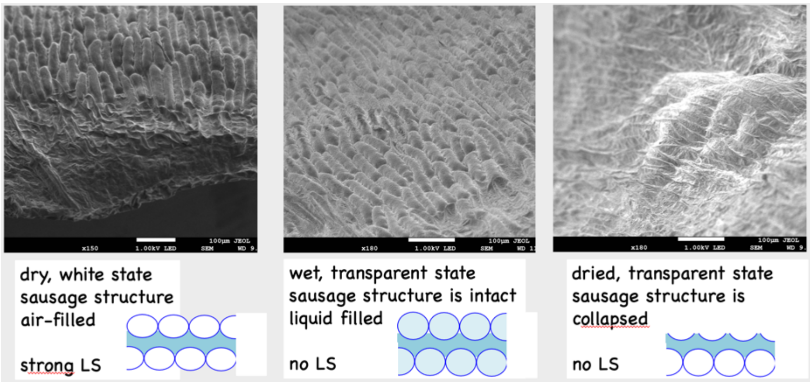

Figure 2: SEM images of dry (left), wet (center), and dried after being wet (right) of D. grayi petals

When we screened other flowers for the same effect, we found that the Japanese Ladybell, Adenophora triphyllium, and also have investigated the infiltration of water into the voids of flower petals by using confocal fluorescence microscopy, of Japanese cherry petals.

4.2. 花弁の生物模倣 Biomimetics of flower petals.

PVDF-HFP is a widely used polymer because it is an amphiphobic highly stable fluorinated polymer that can be used as water filtration membranes. Porous films can be prepared by spin coating or solvent-exchange techniques. Depending on the technique, films with internal pores or asymmetric films with different pore structure on each side of the film can be prepared. Here we perform the solvent exchange reaction on a water surface at higher than room temperature and we observed a clear influence of the water temperature on the change in transparency. Depending on the water temperature during the phase inversion process, the internal void structure has diffent sizes and connectivity.

Thus, at the right conditions, the void structure can be filled with water and a refractive index difference within the film becomes less and the films become transparent. Since the PVDF-HFP polymer has a void structure with stable walls, after drying, the voids keep their shape, the film does not collapse, and it returns to its opaque state, making the transparency change reversible, as can be seen in figure 3 . The transparent-to-white transition just takes a few minutes.

Finally, we were able to measure the refractive index change. Because the fluorinated polymer has a low index, it nicely matches the refractive index of water.

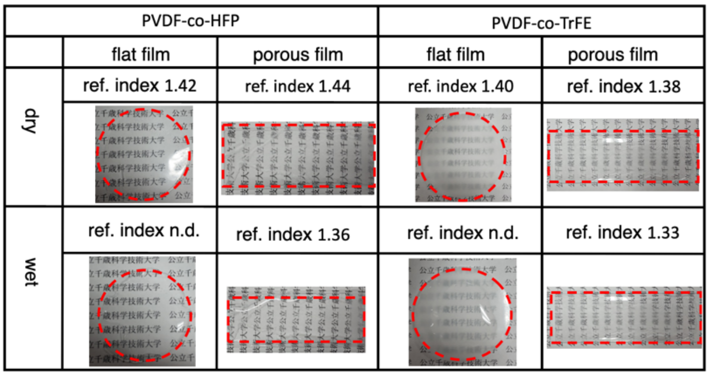

Figure 3: pictures of films in the dry and wet stages and their calculated refractive indices.

Nature still is full of unknown structures and functionalities. One active area where those biological samples are investigated is photonics and optics. The impressive change of transparency in dry and wet flower petals was investigated in this research, and a biomimetic approach to realize a reversible opaque-transparent transition was introduced.
Flower petals use air pockets in or under their endothelial cells to increase light scattering, and by infiltration of water those structures loose the refractive index contrast, and turn transparent. Thin films of porous PVDF-HFP mimic this behavior, and the porous structure could be fine-tuned by adjusting the temperature of the water phase in the phase inversion process to produce porous films.
This research will enable us to produce reversible opaque-transparent thin films with applications in optics and photonics.

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3．雑誌名 Proc. CIF21	6．最初と最後の頁 P13 1-3
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〔図書〕　計0件

〔産業財産権〕

〔その他〕

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6．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考
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7．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

8．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関