White without Titanium-Dioxide

Porous Nanostructures as Replacement for White Pigments

An innovative process allows to fabricate thin, white polymer surfaces without white pigments. For that, the polymer is foamed with supercritical CO_2 resulting in a fine structure of nanobubbles. Film thicknesses of a few 10 µm are sufficient to obtain a perfect white surface.

The white beetle Cyphochilus insulanus is almost completely covered with white scales © Markus Breig, KIT

For all kinds of consumer goods, a bright white surface is frequently desired to convey purity and cleanliness. Titanium dioxide (TiO_2) is the most commonly applied white pigment. It is used in many industrial branches and gives plastic packaging, coatings and paints, as well as food and cosmetics, an opaque and brilliant whiteness [1, 2]. However, rising raw material costs, the labor-intensive extraction and large carbon footprint, as well as the cost-intensive disposal of partly harmful by-products, motivate to replace TiO_2 in white surfaces. In recent years, there has also been growing concern that TiO_2 could be harmful to human health and the environment. In particular nanometer-sized TiO_2 particles are repeatedly criticized [3]. In France, these concerns have led to a ban on TiO_2 as a food additive [4]. In addition, in the long term, TiO_2 could pose a similar problem to that of microplastics, as chemically inert TiO_2 particles could be released finally from the embedding medium and subsequently accumulate in the environment.

Nevertheless, there are many good reasons to use TiO_2 as a white pigment [2]. Some authors and engineers do not see an alternative to this material (see ***Kunststoffe*** *international* 6–7/2019, [5]). Due to their high optical refractive index, TiO_2 particles scatter light particularly effective, since a strong contrast of the optical density the matrix (polymer, binder, »

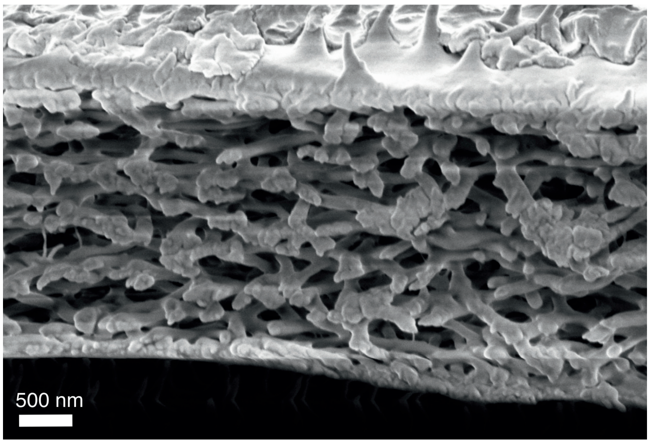

Fig. 1. The scanning electron microscopy image shows the inside of a scale of the white beetle Cyphochilus insulanus. The porous structure consists of chitin and scatters light so well that a layer thickness of only 10 µm is sufficient to make it appear white

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etc.) is achieved. This enables a very effective scattering of all wavelengths of visible light at the interface between medium and TiO$_2$ particles, resulting in a white color impression and good opacity.

However, a look at nature shows that the classical industrial approach to use small particles with high optical density as scattering centers is not the only possible way to effectively scatter light. In nature, there are several examples of white materials where a different scattering mechanism is utilized. Air-filled cavities instead of pigment particles act as scattering centers.

The best-known example of this principle in biophotonics is the white beetle Cyphochilus insulanus (**Title figure**), which originates from Southeast Asia [6, 7]. Its white color probably serves as a camouflage, since it lives in a shady environment on a suitably colored fungus [8]. The upper side of its body is almost completely covered with white scales, which are about 60 µm wide and 200 µm long. The scales are porous inside and consist of a network of fibrous structures (**Fig. 1**). Despite their small thickness of less than 10 µm, the scales scatter light of any wavelength almost perfectly. This effect has been intensively investigated by various groups in recent years and served as a model for the development of scattering materials [9–12].

The example of the beetle Cyphochilus illustrates very well the difference between natural and man-made structures. While engineers often develop solutions using materials consisting of many different chemical elements, the natural ones are usually limited to a single basic material with a rich, complex three-dimensional structure. One can be only amazed by mechanical, optical or physico-chemical properties of such natural solutions. Biomimetics is concerned with understanding, abstracting and imitating the phenomena of nature in order to make them technically usable. Therefore, it often leads to promising approaches which might never have been found in any other way.

Advantages at a Glance

- Coloration solely caused by nanostructuring without any pigments.
- A tiny layer thickness of about 10 µm is sufficient to achieve a high scattering.
- The polymeric material remains pure, which facilitates recycling.

To-Dos till Readiness for Series Production

- To up-scale the demonstrated technology according to manufacturer's needs, for example, for larger films.
- The foamed material cannot directly replace other white pigments in existing production processes. New approaches are required, to apply it as a coating or to add it as a new type of pigment particles into a matrix.

The above described effect found in the beetle's scales can also be reproduced in man-made materials, for example, by introducing in their volume very small, air-filled cavities. This effect can be observed in everyday life by watching soapsuds or sea spray. Light is scattered at the interface between the pore and the surrounding medium such as water or polymer. The high optical density contrast results from the low optical density of air compared to the surrounding medium. The main trick is to make these bubbles tiny enough to enable a technical use as a coating. When the pore size is reduced to a few hundred nanometers, all wavelengths of visible light are scattered effectively, so that even thin layers of the porous material appear white.

Researchers at the Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany, have developed a process for the production of such coatings. For this purpose, polymers are foamed with the aid of supercritical CO$_2$ (**Fig. 2**). As a non-toxic, inert and non-flammable gas, CO$_2$ has become very important not only for foaming, but for various other applications, for example for polymer blending and simplified polymer modification processes (with CO$_2$ as the carrier as well as the swelling agent) or for the production of polymeric particles [14, 17]. This is mainly because it acts as a plasticizer for polymers with good CO$_2$ solubility. Under the influence of CO$_2$ the glass transition temperature of these polymers drops significantly [15]. Due to the good diffusion properties, the gas is often used in the supercritical state at a pressure of over 73.75 bar and a temperature of over 31 °C. This aggregate state lies between liquid and gas state.

White Color due to Foaming

In the process developed at KIT (**Fig. 2**), the polymer is first saturated with CO$_2$ under constant temperature and pressure conditions, typically until the gas concentration in the sample reaches the solubility limit. While CO$_2$ diffuses into the polymer, its glass transition temperature decreases. Under certain conditions, the glass transition temperature is even lower than room temperature [16]. The polymer swells and also becomes viscous if its temperature is higher than the current glass transition temperature.

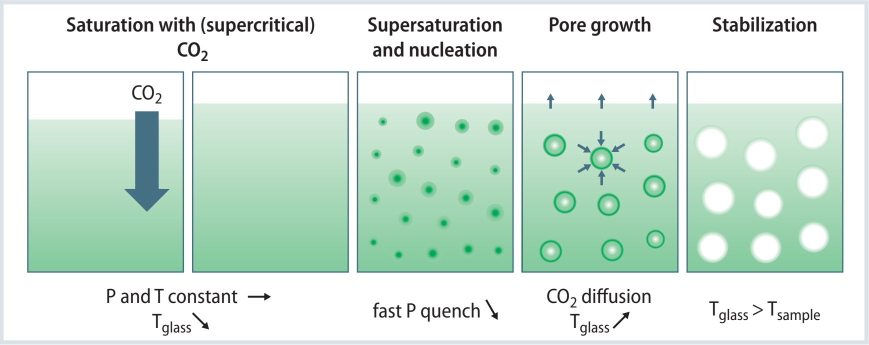

Fig. 2. Foaming with supercritical CO_2 enables the creation of nano-sized pores in polymers such as PMMA. This means that the actually transparent material turns white without adding pigments due to the structure alone Source: Luisa Borgmann, KIT, graphic: © Hanser

In the next step, a sudden drop in pressure induces thermodynamic instability. This leads to a supersaturation of the polymer, whose solubility for CO_2 is much lower under the new conditions. As a result of the supersaturation, nucleation occurs, and for further growth the nuclei must reach a critical size. Now pore growth can take place by diffusion of gas molecules from the polymer matrix into the newly formed nuclei.

While the gas diffuses from the polymer matrix into the growing pores and partly out of the material, the glass transition temperature increases again. The pore structure solidifies when the glass transition temperature has risen to the actual temperature of the sample [17–19]. Due to the foamed porous structure the polymer turns white as shown in **Figure 2** by the example of a previously transparent PMMA film. The pore size and density can be controlled by the process parameters and other process modifications. For example, a higher temperature ensures longer time for pore growth and thus larger pores, while a reduction in pressure moderates the pore density.

The optical spectra in **Figure 3** show how effectively light is scattered at the nanopores. For these examples, thin PMMA films with different, precisely defined layer thicknesses, were applied to a glass substrate and foamed with supercritical CO_2 with optimized parameters. The films were then optically analyzed. The reflection of these films in the visible range is almost constant and increases with the thickness of the foamed PMMA. An effective layer thickness of 9 µm is sufficient to achieve a reflection of approx. 60 %. The effect increases with layer thickness and at a thickness of 79 µm significantly more than 90 % of the incident light is reflected. The inset in the figure shows the inner structure of the film with an effective layer of 9 µm, recorded by scanning electron microscopy (SEM). The pores have diameters of several 100 nm and are distributed irregularly in the polymer.

The right graph in **Figure 3** compares the scattering of the foamed PMMA films with white paper, so-called "photonic glass", and the scales of the Cyphochilius beetle. The transmission of light is plotted as a function of the inverse material thickness. This so-called "Ohm's law for light" gives an indication of the mean free path length of light and thus allows a simple comparison between different materials [7, 11]. With this method, the curve for white paper has the steepest slope, while the curve for "photonic glass" is much flatter. The scales of the white beetle enable the most effective scattering in our comparison and the corresponding curve is very flat, since the mean free path of light scattering is only about 1.47 µm. The foamed PMMA films perform slightly worse than "photonic glass", but much better than white paper. For the human eye, a film of only 10 µm thickness already appears perfectly white.

Suitable for PMMA, TPU and PLA

The presented process successfully avoids the need for potentially harmful pigments by creating porous polymeric structures. Just like the bubbles of shaving or bath foam, the structure of these also scatters light, making the materi- »

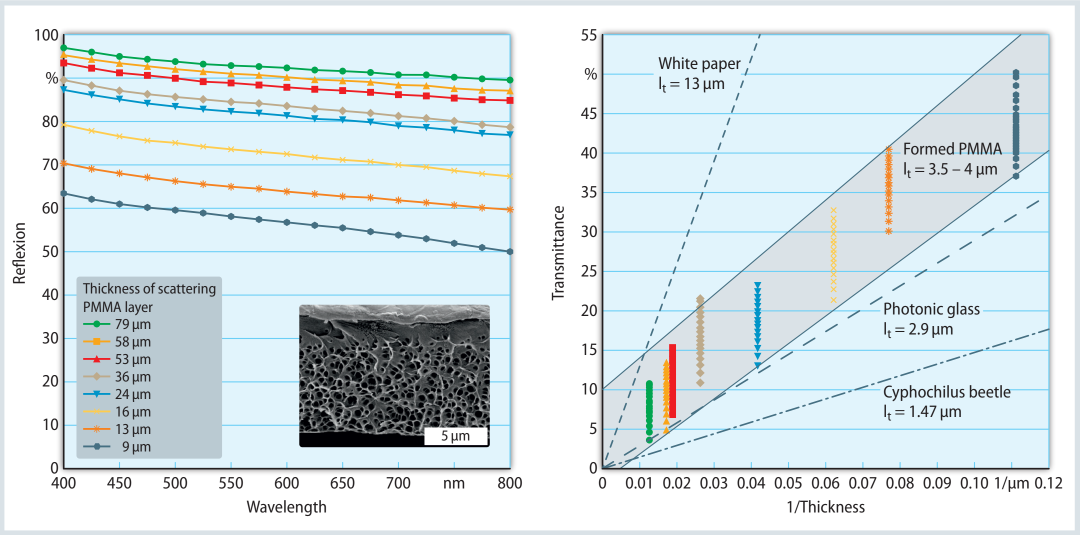

Fig. 3. The graph on the left shows the reflection as a function of wavelength for different film thicknesses. The SEM image shows the inner structure of an approx. 10 µm thick foamed PMMA film. The graph on the right compares the foamed PMMA films with other white materials Source: Julia Syurik, KIT, graphic: © Hanser

al appear white. The technique is inexpensive and suits not only for PMMA but also for various thermoplastics such as thermoplastic polyurethanes (TPU) and biodegradable polylactides (PLA).

The thin polymer films are very flexible and light. Although nanostructuring changes the elastic properties of the material, the films are mechanically stable enough [20] to be thermoformed and applied as a coating to various surfaces [11].

Foaming with supercritical CO_2 does not leave any residues of solvents, as the process of generating a pore structure is purely physical. Accordingly, there is great potential in applications where solvent residues are to be avoided and where TiO_2 alternatives are particularly in demand, for example in food and cosmetics packaging. The increasing demand for efficient recycling of products is another advantage, as the inserted pores are much easier to reverse than embedded particles. If the polymer is heated accordingly, the nanobubbles disappear without residue. Furthermore, the localized heating above the material's glass transition temperature allows the white films to become locally transparent again and can be beneficial for ink-free stamping or counterfeit protection.

Since many white consumer goods from packaging to furniture surfaces are made of polymers or polymeric coatings with added TiO_2, there is a wide range of applications for the foamed films. In addition, there is a growing willingness to replace TiO_2 particles. On the one hand this is desired by end users and on the other hand by manufacturers expecting further legal restrictions for TiO_2 usage in the future.

However, the foamed material is not a 1:1 replacement for TiO_2 or other white pigments. It requires new approaches to apply the foamed polymer as a film. Instead of using complete polymer coatings or foils, foamed particles could also be introduced into a plastic matrix. **Figure 4** shows that particles can also be foamed: an originally transparent particle of PMMA appears white after foaming. This technique can also be used to whiten materials that cannot be foamed directly. ■

The Authors

Luisa Borgmann, M.Sc., has been working on the further development of the method in her PhD at KIT since 2019.

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Service

References & Digital Version

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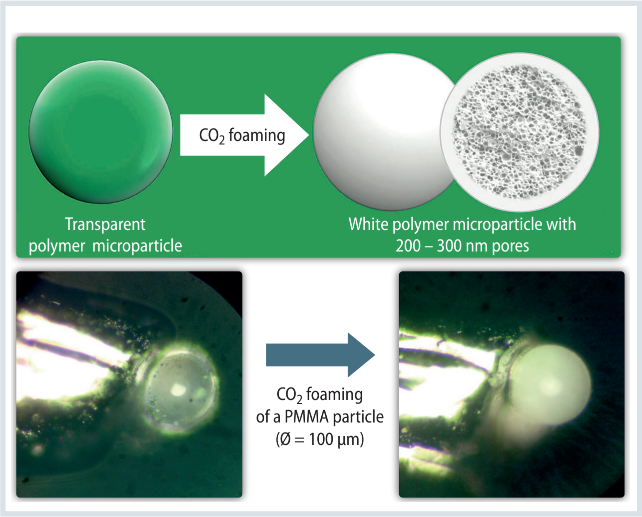

Fig. 4. The process is also suitable for foaming PMMA particles. In the future, these particles will be further tested for their suitability as pigments Source: Luisa Borgmann, KIT, graphic: © Hanser