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PROTECTION FOR BIOPLASTICS

Biodegradable hybrid lacquers improve durability and barrier properties. By Sabine Amberg-Schwab, Daniela Collin and Johannes Schwaiger.

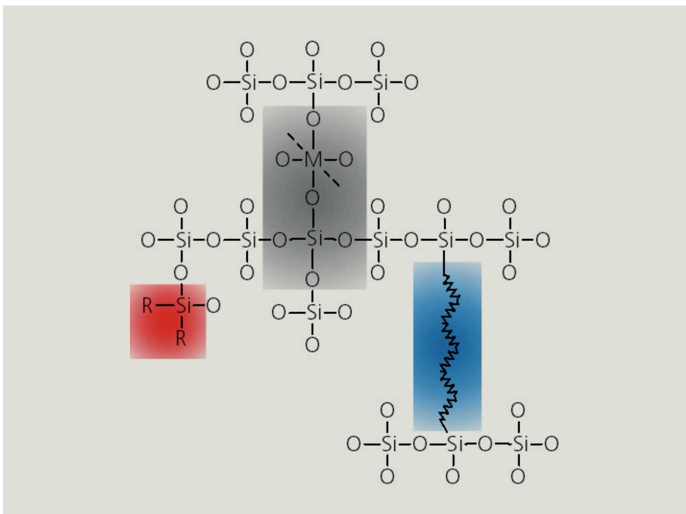
The properties of biodegradable plastic films can be improved by applying biodegradable hybrid coatings. Biodegradable products suitable for high-quality food packaging were created, with good barrier properties against water vapour and oxygen, and a moisture-triggered antimicrobial system.

Biodegradable plastics offer the potential for creating a more sustainable society and solving global environmental and waste problems. However, few products made of biodegradable plastics have so far become established in the marketplace.
A well-known example product is symptomatic of the problem here: biodegradable bags for bio-waste, which are available in many supermarkets. Whilst these bags are able to hold the solid waste for a certain time, moisture from the bio-waste is gradually absorbed by the bags, finally causing the bag to fail.
The properties of the bags, like those of other biodegradable plastics, often do not meet all the desired requirements and are still inferior to those of established non-biodegradable plastic products. Also, biopolymers have so far had only limited use as high-quality packaging materials for foods. This is because they do not provide sufficient protection for foods against oxygen and water vapour penetration and so cannot guarantee the required shelf life.
The modification of biodegradable polymer films with a biodegradable coating to improve their properties could in future lead to the use of these biopolymer systems for food packaging. Based on hybrid polymer coating materials, many of which have excellent barrier properties [1], biodegradable coating materials have now been developed which can also be applied as lacquers.
The development work focused on the barrier properties to water vapour and oxygen and on moisture-triggered antimicrobial properties. In order to obtain these properties, state-of-the-art hybrid polymer barrier coatings, which have been developed at the Fraunhofer-Institute for Silicate Research over many years, were modified and functionalised with special components to make the coatings biodegradable.

THE STARTING POINT: ADVANCED HYBRID COATING POLYMERS

"Ormocers", the hybrid polymers developed by the Fraunhofer Institute for Silicate Research ISC in Würzburg, consist of a combination of organic and inorganic components [2]. These hybrid polymers enable the properties of glass and plastic to be combined, with new innovative combinations of features being achieved by synergistic effects [2, 3].
The sol-gel method which is used for synthesising these hybrid materials starts off with inorganic and organic-inorganic precursor molecules [4]. Controlled hydrolysis and condensation reactions of organo-alkoxysilanes and metal alkoxides produce the inorganic network of the hybrid polymer.
The organic network forms via subsequent polymerisation of reactive organic groups, which are introduced via the organo alkoxysilanes. Typically, this involves epoxide polymerisation or radical polymerisation of acrylates or methacrylates.
The organic network formation and hence the curing of the material can be induced by heat or UV light. In addition, organic modification of

Figure 1: Structure of "Ormocer" hybrid polymers: oxidic inorganic network (area shaded grey, M = Si, Al, Ti, Zr, etc.), organic modification of the inorganic network (shaded red), and organic network (shaded blue) according to [3].



RESULTS AT A GLANCE

→ Innovative functional coating materials have been developed to improve the properties of biodegradable plastic films, which often show performance limitations.

→ The biodegradation time can be adjusted and so customised for different food packaging or other requirements.

→ The new coatings can provide very good barriers to oxygen and water vapour when used in combination with a vapour-deposited silica layer.

→ Biodegradable coating systems with a moisture-triggered antimicrobial effect were also developed.

→ Future developments in this field will also focus on tailoring the new biodegradable coatings for other areas of application.

the inorganic network is possible by introducing non-reactive organoalkoxysilanes.
The cured hybrid polymer network is shown schematically in *Figure 1*. The grey-shaded area represents hydrolysed and/or condensed components which form the inorganic network and have silicon and other heteroatoms incorporated into the oxide network. The organic network (blue-shaded area) and organic modification of the inorganic components (red-shaded area) are also shown.
This type of hybrid polymer is often used for coatings [5] for a wide range of different applications. Examples include photochromic and electrochromic coatings [6], scratch-resistant and abrasion-resistant coatings [7] and also hydrophilic, hydrophobic, coloured [8], antimicrobial [9] and antistatic coatings [10]. Hybrid polymer coatings in combination with inorganic layers are suitable for packaging food [1] and for the flexible encapsulation of opto-electronic systems [11].
Until now none of these coatings could be used with biodegradable plastics because the hybrid polymers themselves were not degradable. The work described here aimed to incorporate biodegradability into these materials, whilst maintaining their excellent barrier properties. An additional aim was to introduce a moisture-triggered antimicrobial effect.

HOW THE HYBRID POLYMERS WERE MADE BIODEGRADABLE

The development of biodegradable hybrid polymer coatings ("BioOrmocers") was achieved by replacing the non-biodegradable organic components with biodegradable components. Both bio-based biodegradable natural materials (chitosan, cellulose derivatives) and petroleum-based biodegradable reactants (e.g. polycaprolactone-triol (PCL-T)) were used for this.
In order to guarantee incorporation of the biodegradable components into the hybrid polymer network, some of these components were subjected to chemical modification. For example, the polycaprolactone derivative was functionalised with triethoxysilane groups [12], in order to subsequently allow attachment of these biodegradable components to the inorganic network via hydrolysis and condensation reactions.
The cellulose was treated similarly. In this case, attachment of biodegradable precursors to the organic network of the hybrid material was achieved by functionalisation with epoxy groups. The reactive epoxy groups subsequently participated in the polymerisation reactions for formation of the organic network. In contrast, chitosan required no modification because it can link with the organic network via some of its own amino groups.
All the modified materials showed successful attachment of the biodegradable components to the hybrid polymer network, as demonstrated by spectroscopic methods. The inorganic network was analysed using ^{29}Si solid state NMR and Raman spectroscopy, whilst the organic network was analysed using ^{13}C solid state NMR and Raman spectroscopy.
The structure of the hybrid polymer "BioOrmocer" network is shown in *Figure 2*. The inorganic and organic network components are once again shown in grey and blue shaded areas respectively. However, the

Figure 2: Structure of hybrid polymer "BioOrmocers": oxidic inorganic network (area shaded grey, M = Si, Al, Ti, Zr, etc.), organic network (shaded blue), biodegradable fraction (dark green: linked to the inorganic network; light green: linked to the organic network).

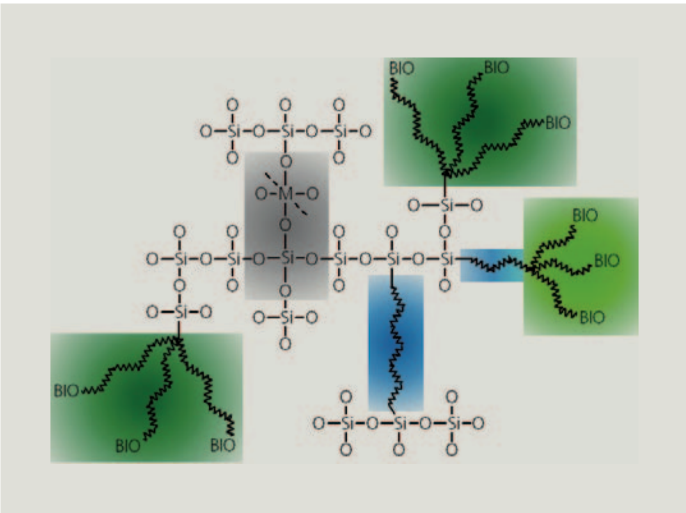


Figure 3: Appearance of coatings containing biopolymer with (a) 30 wt.% chitosan and (b) 45 wt.% PCL-T on PET substrates.

structure now has biodegradable components attached to either the inorganic network (dark green area) or to the organic network (light green area).

GOOD APPEARANCE AND BIODEGRADABILITY

Below, two of these new biodegradable hybrid polymer coating systems are described in more detail. One system involves incorporation of a PCL-T component into the coating matrix via attachment to the inorganic network. The other involves incorporation of a chitosan compound into the coating matrix via attachment to the organic network. Both systems showed very promising results with regards to appearance, biodegradability, barrier properties and moisture-triggered antimicrobial effect.

Flawless optical properties are required for packaging materials. *Figure 3* shows the appearance of two example coatings on a polyethylene terephthalate (PET) substrate.

All the coatings with PCL-T and chitosan had a transparent, smooth and homogeneous surface with no defects. The coatings showed good adhesion to the substrate and the same good optical quality independent of the selected biopolymer content.

The biodegradability of the coatings was tested by storing the samples in a test compost. For this, the newly developed hybrid polymer coatings were applied to non-degradable substrates made of polyethylene terephthalate (PET). This procedure ensured that any observed biodegradation was not due to the substrate.

Degradation was visible to the naked eye after just six weeks in the compost for the samples containing either PCL-T or chitosan. These observations were confirmed by images taken with a laser scanning microscope and scanning electron microscope (SEM). *Figure 4* shows, as an example, an SEM image of a coating containing 30 wt.% chitosan before and after storage in the compost, along with an image of a state-of-the-art non-biodegradable hybrid polymer coating.

Variation of the biopolymer content also allowed customisation of the degradation rate. The amount and choice of biopolymer thus enable the rate of degradation to be controlled.

BARRIER PROPERTIES ACHIEVED VIA VAPOUR DEPOSITION

Food packaging materials must possess particularly good barriers to odours, water vapour and oxygen for use with sensitive products such as coffee [13]. Adaptation of the network density and polarity of the hybrid polymer coating material and combination with inorganic oxide

Figure 4: Scanning electron microscope images of (a) a biodegradable coating containing 30 wt.% chitosan and (b) a state-of-the-art non-biodegradable hybrid polymer coating, in both cases before and after storage in compost.

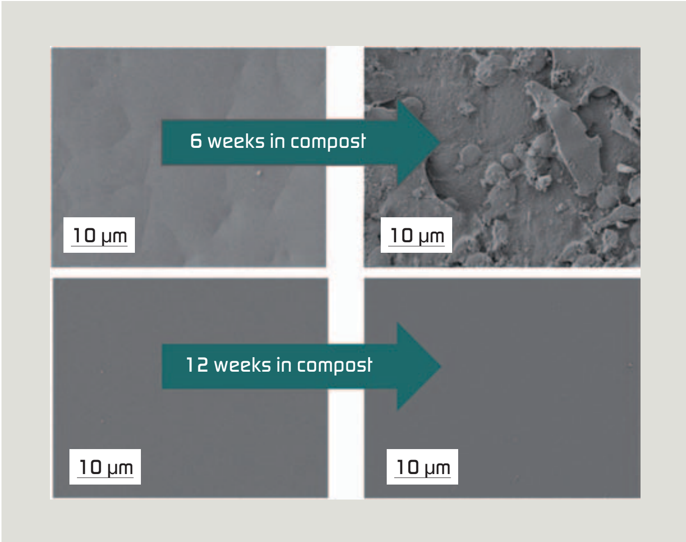


Figure 5: Oxygen transmission rate (OTR, at 50% r.h. and 23 °C) and water vapour transmission rate (WVTR, at 90% r.h. and 38 °C) for the chitosan and PCL-T containing coatings in a layer system comprising PET film and SiOx layer; the orange line indicates the barrier requirement for food packaging.

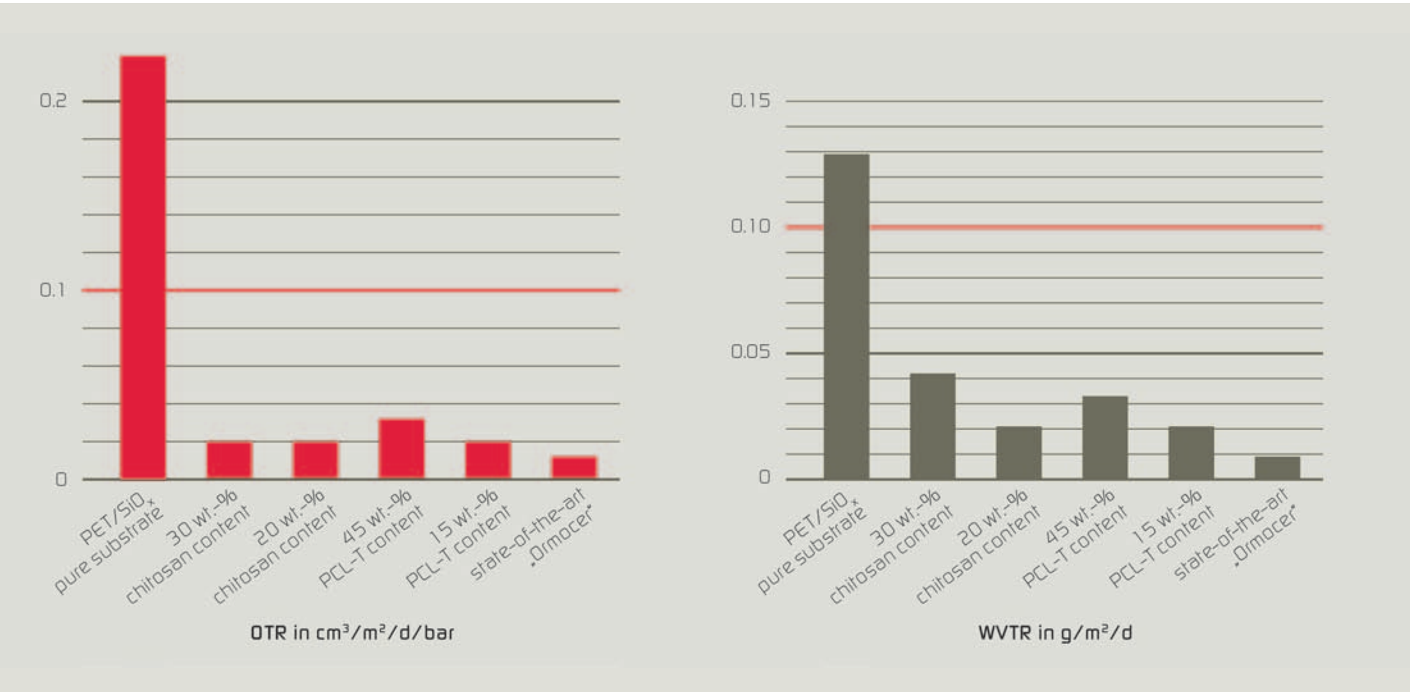
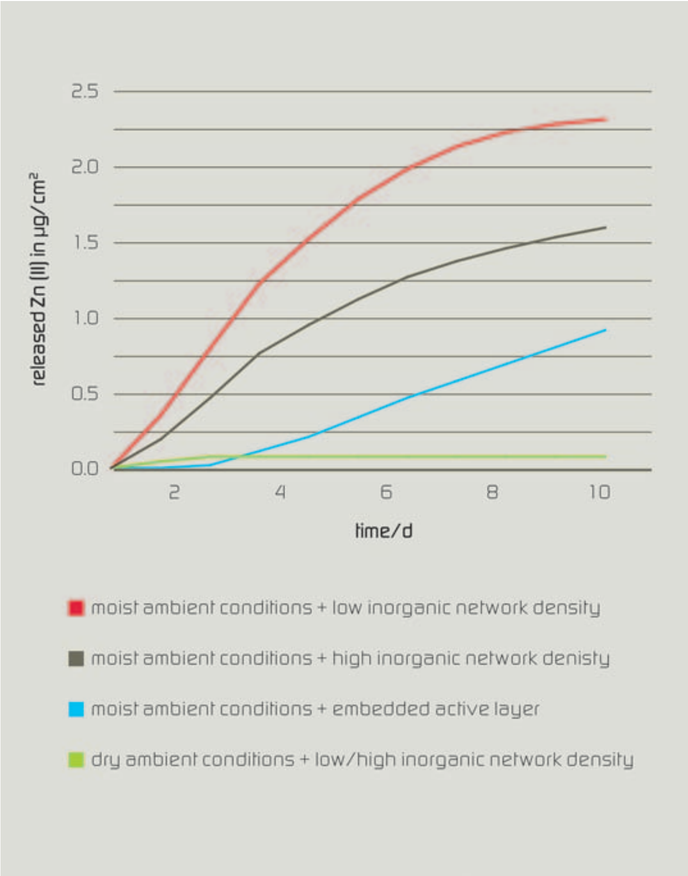


Figure 6: Cumulative amount of Zn(II) ions released under moist (80% RH - blue, green, black) and dry storage conditions (20% RH - red) for different polymer systems.



layers such as SiO_x (where $1.5 < x < 1.8$) allow very good barrier values to be achieved [1].

There are synergistic effects between the hybrid polymer coating and the vapour-deposited SiO_x layer. The hybrid polymer coating lowers the micro/nano porosity of the SiO_x layer and fills defects. Covalent Si-O-Si bonds also form between the SiO_x layer and the hybrid polymer [14], leading to a high inorganic network density in the interface region. These two effects only occur together and in the interface region of the two layers. This means excellent barrier properties are achieved independent of layer thickness [13].

By combining a SiO_x layer with the new biodegradable hybrid polymer coatings, barrier values are achieved which easily meet the requirements for food packaging (namely 0.1 $cm^3/m^2/d/bar$ for oxygen and 0.1 $g/m^2/d$ for water vapour [15]).

Figure 5 compares the barrier values for a PET film with SiO_x layer to those for the newly developed coatings (structure: PET/SiO_x/biodegradable hybrid polymer coating). For reference, the results for a state-of-the-art barrier coating are shown. The orange lines indicate the minimum requirements for food packaging.

The different biodegradable coating systems having differing biopolymer contents possessed excellent barriers to oxygen and water vapour and clearly met the requirements for food packaging.

BENEFITS OF A MOISTURE-TRIGGERED ANTIMICROBIAL EFFECT

In addition to their biodegradability and barrier properties, the hybrid polymer coatings containing PCL-T were specifically designed with a moisture-triggered antimicrobial effect.

If the packaging material is stored dry, no antimicrobial substances are released and hence lost from the system. Only when the packaging material is used for foods having a certain moisture content is the antimicrobial effect triggered by the moisture in the food, with no loss of effectiveness on storage and the full antimicrobial effect consequently being available.

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The incorporation of antimicrobial Zn(II) ions [16] and control of the swelling properties of the coating by adjusting the network densities made it possible to achieve controllable moisture-triggered release of antimicrobial Zn(II) ions.
Zn(II) ions are an essential trace element for the human metabolism. The European Food Safety Authority recommends a zinc intake of 25 mg per day for adults [17]. The use of zinc in food packaging thus makes sense, but the prescribed limit values must not be exceeded. *Figure 6* shows the release of Zn(II) ions as a function of time from different hybrid polymer coating systems under moist (80% relative humidity - blue, green, black) and dry ambient conditions (20% relative humidity- red). The graph shows coating systems with both low (blue curve) and high (green curve) inorganic network densities. Also shown is a delayed release due to embedding the active layer (packaging layer structure - black curve in the figure).
Both the duration of the moisture-triggered release and the amount of antimicrobial Zn(II) ions released were dependent on the storage conditions (temperature and relative humidity) and correlated with the inorganic network density of the biodegradable hybrid polymer coatings. It was thus possible to adjust the rate of release and the amount of antimicrobial additive released under different ambient conditions by selecting a suitable hybrid polymer coating system.

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“The resulting coatings exhibit good adhesion and transparency as well as excellent barrier properties.“

2 questions to Dr Sabine Amberg-Schwab

How did you apply the coating in the lab? *We used a spiral applicator for our lab coating trials. We also did some tests on a roll-to-roll coating machine.*

In how far would the consumer and the industry benefit from this coating? *The aim of our work was to modify our state-of-the art “Ormocers” to be biodegradable and likewise preserve the barrier and functional properties and thus to provide new barrier materials for functional biodegradable packaging. This was achieved by the incorporation and chemical linkage of chemically modified biopolymers within the “Ormocers”. The resulting coatings exhibit good adhesion and transparency as well as excellent barrier properties. They also show an adjustable temporal process of biodegradation. These new materials can play a part in the future design and development of new innovative and more environmental-friendly packaging materials.*

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