

Polymers at Surfaces and Interfaces at ZHW

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Abstract: The properties of solids and liquids are strongly influenced by surface phenomena. At the interface of two phases, properties like wetting, adhesion and friction are determined by the degree of interaction between the phases. Controlling this interaction by means of chemistry at interfaces represents the major research topic of the Laboratory of Industrial Chemistry at ZHW.

Keywords: Blends, Coatings, Composites, Interfaces, Polymers

In April 2004 *Martina Hirayama* was appointed head of the Laboratory of Industrial Chemistry at ZHW as successor of Heiner Bührer. The main activities of the group have been and will be in the field of polymer science and technology. The new focus is on polymers at surfaces and interfaces. This article gives an overview of the different R&D activities in the Laboratory of Industrial Chemistry.

Polymeric Nanocomposites

The principle of using inorganic fillers to reinforce a polymer matrix is well established. However, recent research concentrates on nanosized fillers with a higher specific surface area to interact with the polymer matrix. Incorporation of suitable nanofillers into a polymeric matrix can lead to an improvement in mechanical, optical, and electrical properties.

Layered silicates have been the subject of many studies. They contain exchangeable interlayer and surface ions. Since unmodified layered silicates hardly disperse in polymers, the sodium and calcium cations of the layered silicates need to be replaced by organic cations, *e.g.* organoammonium compounds. The cation exchange on the one hand separates the silicate layers giving a suitable plate-like nanofiller. On the other hand, the organic cations render the resulting organosilicate organophilic enough to be homogeneously dispersed in the polymer [1]. Depending on the size of the organic cations used for ion exchange, intercalation of the polymer into the silicate layers for small cations or a complete separation of the silicate layers for large cations (exfoliation) may occur (Fig. 1a). Although many studies on ion exchange of layered silicates can be found in literature, the temperature stability of the modified layered silicates is still a problem. We currently investigate together with EMS-Chemie AG the ion exchange of layered silicates targeting enhanced temperature stability together with enhanced mechanical properties and reduced permeability to gases of polyamide composites.

Also SiO₂, TiO₂, ZnO and other inorganic particles are widely used as fillers. In a current project we reinforce a poly(dimethylsiloxane)-based polymer with silica

nanoparticles. The filler is expected to have two beneficial effects, namely a better abrasion resistance of the intrinsically soft material and a nanostructured surface leading to a hydrophobic effect (lotus effect). In order to disperse the silica nanoparticles in the polymer matrix, their surface is chemically modified (Fig. 1b). Since the material should be transparent, the silica particles have to be homogeneously dispersed to avoid agglomeration which causes significant scattering of light.

Beside technical polymeric composites, nature gives some outstanding examples of successful composite materials, *e.g.* teeth and bones in mammals and marine diatoms (Fig. 1c). Biological composites generally consist of a matrix, formed by organic macromolecules like collagen or chitin, and a mineral phase like calcium carbonate, silicon dioxide or apatite [2]. Considering the high performance of these materials and the capability of nature to perfectly control nucleation and crystal growth, biomimetic approaches to composites are a new and challenging field of research in our group.

Polymer Blends

Mixing two polymers in order to obtain materials with new properties represents

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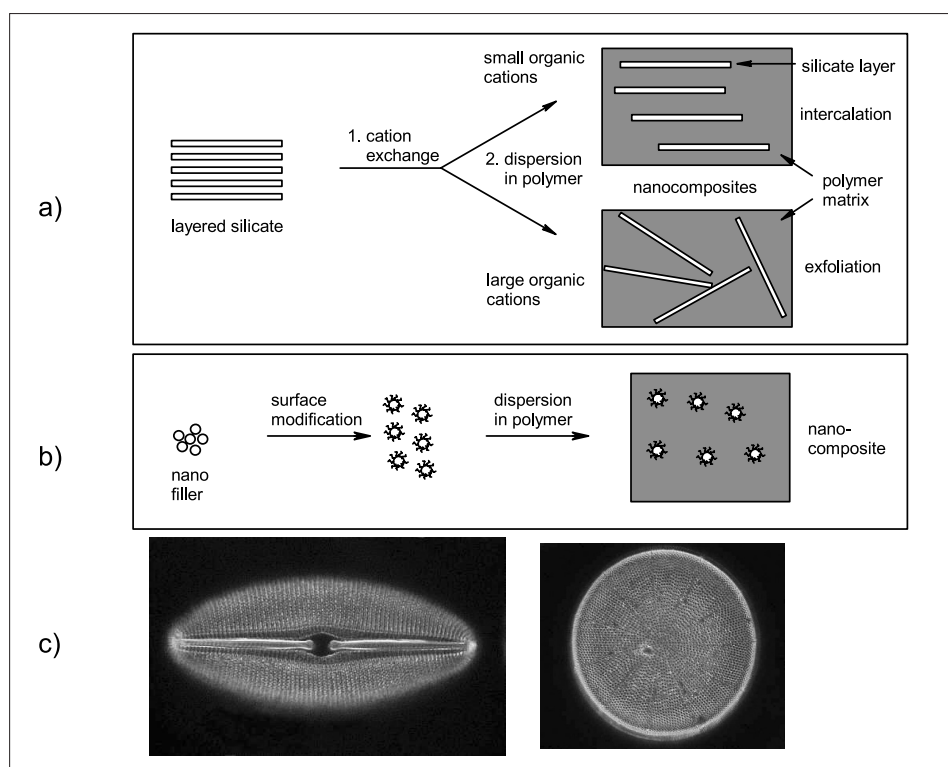


Fig. 1. Different approaches to nanocomposites: a) from layered silicates *via* cation exchange to dispersion in the polymer (top), b) from nanofillers *via* surface modification to dispersion in the polymer (middle), c) diatoms as an example for biological composites (bottom, pictures from <http://www.diatomeen.de>)

another research area where interfaces play a dominant role. Most polymers are partially miscible. Partially miscible polymer blends are characterized by the occurrence of homogeneous or multi-phase microstructures depending on the prevailing conditions of composition, temperature, pressure, and flow. In the case of multi-phase microstructures, the mechanical properties strongly depend on the interaction at the interface between the phases. With a low degree of interaction, the interlayer becomes very thin (<1 nm) so that there is no anchoring effect interlocking the phases. This problem may be overcome using compatibilizers. These compatibilizers are often copolymers having two segments: one segment is thermodynamically miscible or able to cocrystallize with the first polymer, the other segment with the second polymer [3]. Synthesis of compatibilizers as well as blend processing and characterization is done in our laboratory to obtain materials with new properties.

Phase separation within a polymer blend may also be of advantage. For example, nanophase-separated polystyrene/poly-methylmethacrylate coatings on glass give access to nanoporous films with excellent antireflecting properties after washing out the polystyrene phase [4]. The removal of the polystyrene creates holes with a diameter of ca. 100 nm in the remaining polymethylmethacrylate film, leading to practically no discernible reflection of light while the surface still has a high optical transmission.

Phase separation within polymer blends commonly leads to disordered, isotropic structures. However, it has been shown that a two-component polymer film, *e.g.* (polystyrene/polyvinylpyridine) can be guided into arbitrary structures when coated on a substrate with a prepatterned variation of surface energies [5]. This technique may find applications in the field of microelectric circuits and lithographic semiconductor processing.

Since the occurrence of homogeneous or multi-phase microstructures depends on temperature, we are interested in the use of these structures as smart materials.

Coatings

Coatings allow to readily change the surface properties of solids such as wetting, adhesion, friction, wear, biocompatibility, abrasion resistance, permeability to gases and light reflection. The formation of ultrathin layers by adsorption from solution of organic compounds has been investigated with growing interest in the past decade.

Poly(siloxane)s are widely used in coating technology, *e.g.* as water-repellant, anti-stick, or lubricating layers. However, the application methods are often connected with difficulties, in particular in the context of the manufacture of thin films. We have developed a novel, versatile method which allows the preparation of ultrathin, homogeneous and strongly adhering siloxane

layers to the surfaces of various materials, such as metals, metal alloys, glasses, silicon wafers, ceramics, rock, artificial stone, wood, paper, textiles, and plastics [6–9]. The related layers are simply prepared by using solutions with the siloxane containing Si–H bonds and an activator. The layer thicknesses finally obtained are in the range of a few nanometers, *i.e.* a monolayer. Depending on the polymer used for coating hydrophobic layers (Fig. 2) as well as adhesion promotion layers to a variety of polymers can be obtained [8–10].

Calcification on surfaces is a great problem for a variety of applications. We currently investigate in corporation with Geberit AG anti-calcification coatings, based on functional polymeric nanolayers. Beside the common approach of structured super-hydrophobic coatings we investigate the effect of polymers known to have an influence on the crystallization of calcium carbonate. Controlled deposition of minerals is a common issue in biomineralization [2]. Hence a biomimetic approach by coating suitable polymers, influencing the crystal growth and nucleation of calcium carbonate, onto the surface seems to be promising. The coating may not only have an impact on the amount of scale, but also on the adhesion and the polymorphism of calcium carbonate.

Smart coatings attract increasing attention. We are interested in polymeric nanocoatings with incorporated photochromic dyes like azobenzene. The photoisomerization of the azobenzene is used to induce changes in the properties of the polymers. A polymer able to switch from a hydrophobic to a hydrophilic property would be an interesting material.

Ultrathin layers can also be obtained from compounds with low molecular weight. Among these, self-assembled monolayers (SAMs) are of special interest [11][12]. In particular sulfur-containing compounds such as alkanethiols, dialkyl disulfides, and thioethers on gold, fatty acids on metal oxide surfaces and alkyltrichlorosilanes on glass were studied. All of these films distinguish themselves by a controlled thickness and a strong adsorption between the substrate and the head group of the selected organic molecule. Van der Waals' interactions between the alkyl moieties within the films ensure tight packing and stability of the monolayers, making them suitable for applications such as change of wettability, friction and semiconductor passivation. Applying bifunctional molecules permits a derivatization of the surface of the SAM (Fig 3). This kind of functionalized films finds applications, *e.g.* in biomolecular electronics and biosensor development.

Another type of coating, which attracts our interest, is based on sol–gel processes. After hydrolysis and condensation of the pre-

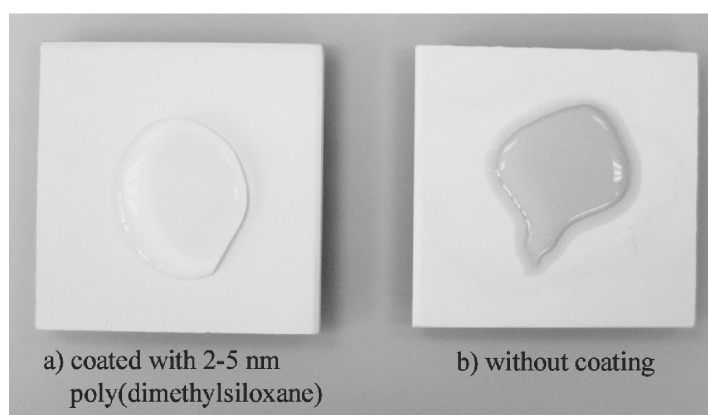


Fig. 2. Water on clay plates a) with a water repellent 2–5 nm thin poly(dimethylsiloxane) coating b) without coating

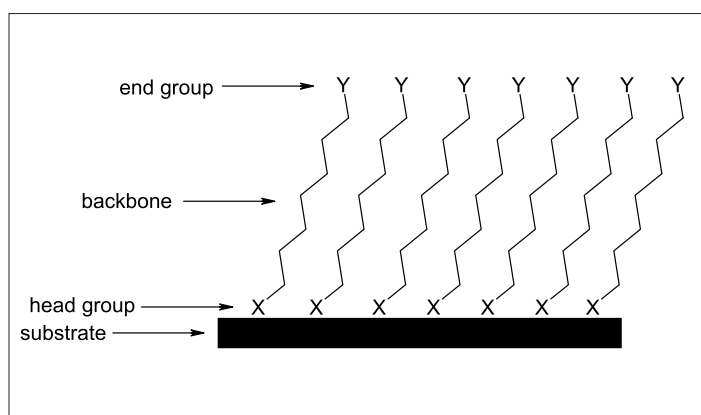


Fig. 3. Schematic representation of a self-assembled monolayer of bifunctional molecules

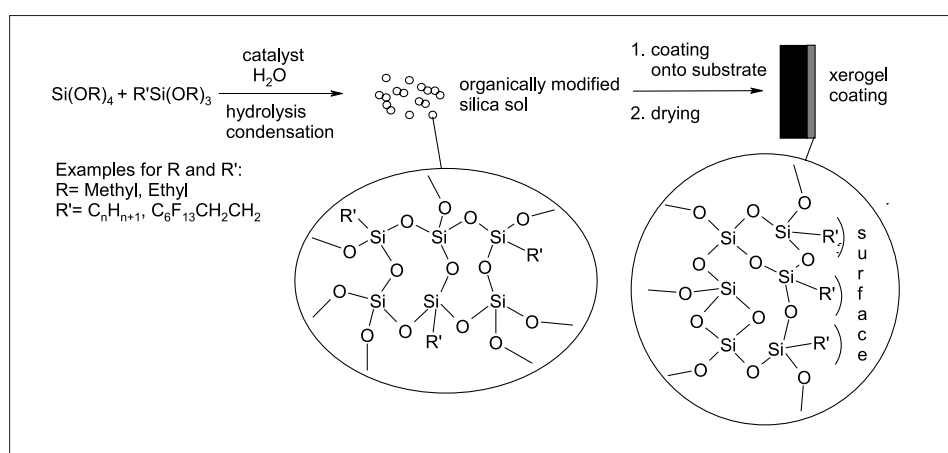


Fig. 4. Schematic representation for the preparation of an organically modified xerogel coating. R' is enriched at the surface of the dried xerogel and therefore allows to drastically change surface properties like surface energy.

cursors, the resulting sol can be applied onto surfaces *via* dip coating or brushing. Drying at low temperatures gives xerogel films whereas calcination at temperatures above 500 °C results in the formation of ceramic materials or glasses [13]. The research in our group in this area focuses on the development of abrasion resistant hydro- and oleophobic coatings as well as on hydrophilic coatings, which we currently investigate in a project. In order to obtain the desired properties of the coating, silica sols are organically modified using trialkoxysilanes bearing an additional functional group (Fig. 4). During the sol–gel process, these organic groups are incorporated into the sol and allow to adjust the surface behavior as well as the bulk properties of the dried xerogel.

Collaborations

Besides the collaboration with other groups at ZHW, especially at the School of Engineering and the Institute of Chemistry and Biotechnology (ICB) [14], we cooperate with groups at ETH Zürich [15], other universities, EMPA [16], MatNet [17] and in-

dustry, which allows us to work on challenging interdisciplinary projects. The R&D projects can be with various partners, financed for example by industry and KTI/CTI [18] or bilateral in particular with industry. Small projects can be carried out during student projects or diploma theses. In addition we support industry with our infrastructure and specialized know-how.

Teaching

The unity of teaching and research by the transfer of R&D into teaching in advanced courses as well as in student projects and diploma theses, allows our students to develop creative practical solutions for interdisciplinary problems.

Together with the EMPA, the University of Applied Sciences Vorarlberg (FHV) and the Interstate University of Applied Sciences of Technology Buchs (NTB) the ZHW actively participates in the interdisciplinary Micro and Nanotechnology Network of the Euregio Bodensee dedicated to knowledge transfer. The first product emerged from the network is a master course

in micro and nanotechnology, which started in autumn 2004.

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