



COATINGS GO TO WORK

An overview of today's functional coatings. By Dr Jamil Baghdachi.

Coatings can have functionality beyond their protection and decoration of substrates. Functional coatings additionally offer a variety of smart behaviours and value-adding performance to a surface. This overview explains the underlying physical and/or chemical processes for a few key types.

Traditionally, the primary functions of coatings are to protect and decorate substrates. More recently, growth has occurred in the research and development, as well as commercialisation, of coatings which have novel functions in addition to having traditional protection

Figure 1: Liquid contact states illuminate superhydrophobic surfaces.

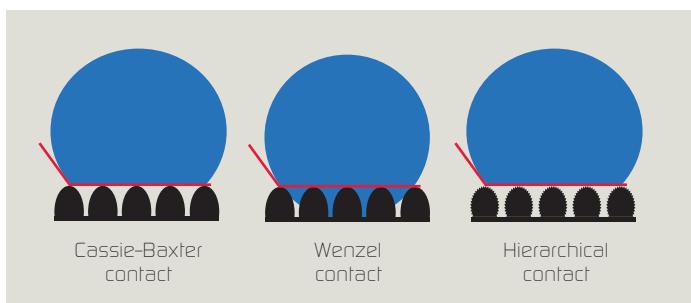
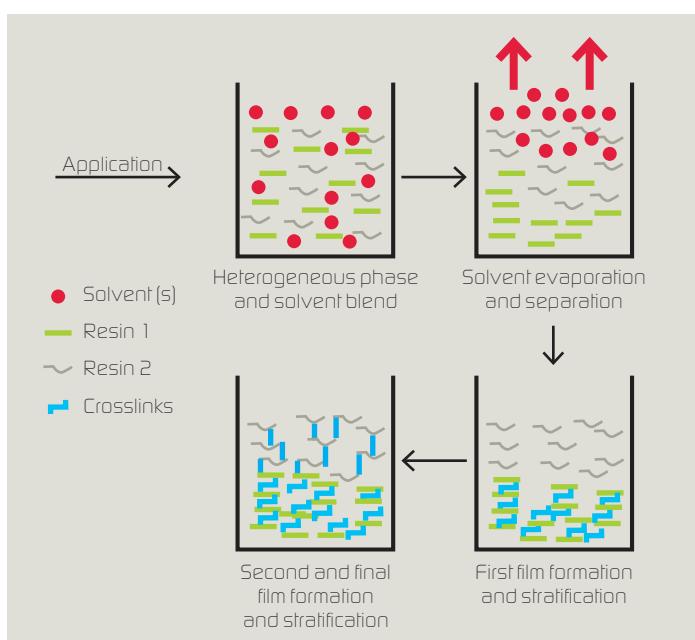


Figure 2: Schematic representation of kinetically controlled self-stratifying coating structure from initially homogeneous solutions of incompatible polymer blends.



and decoration properties. These coatings are often referred to as functional coatings. Materials such as thermochromic, energy efficient coatings for buildings and antireflective coatings for eye glasses have been commercially available for nearly two decades. These classes of coatings generally provide significant added value. In general, they provide their function in three distinct zones: at the interface of the coating and air, in the bulk of the coating, and at the interface of coating and substrate. While the list of functional coatings is long, examples of some of the commercial and most recognisable functional coatings are: antifouling, antimicrobial, colour shifting, conductive, easy-clean, photo- and thermochromic, self-healing and superhydrophobic coatings.

SCIENCE AND TECHNOLOGY OF FUNCTIONAL COATINGS

All coatings have surface functionalities. The standard properties of adhesion, corrosion and scratch resistance, gloss, hydrophobicity, antimicrobial, etc., are properties of the surface rather than of the bulk. Bulk properties are those such as cohesive strength, low gas and moisture permeability, and general durability.

Broadly speaking, all conventional coatings are also functional except that their function is either limited or fixed to a particular property. For this reason, functional coatings or multi-functional coatings share many of the compositional concepts and formulation guidelines of ordinary coatings. Therefore, functional coatings must possess similar basic properties to conventional coatings and use similar ingredients, in addition to other, specific materials.

In general, the unique features of functional coatings, whether surface functionality, or bulk, are brought about by the following three classes of materials: specifically designed responsive polymers; responsive additives, diluents, or solvents; and responsive pigments. Material selection is often one of the most important parts of the coating formulation. Simply incorporating a responsive ingredient in a conventional coating formulation will not result in a functional coating. Functional coatings as a group can be divided into two classes with different,

distinct functions. First, those coatings that are intrinsically functional, such as superhydrophobic, antimicrobial, antifouling, antireflective radar absorbing, self-stratifying, or conductive coatings. Second, the class that is extrinsic or stimuli responsive and function by specific external or internal triggering mechanisms. This class includes coatings such as thermochromic, colour shifting, touch sensitive, corrosion- and explosive-resistant, self-healing and shape-memory materials.

ANTIMICROBIAL COATINGS

Coatings can be designed to kill or inhibit the growth of bacteria through three mechanisms: (1) coatings that can resist the attachment of bacteria, (2) coatings that release biocides that will kill the bacteria, and (3) coatings that can kill bacteria on contact. Coatings can also combine two or more of these mechanisms [1, 2].

To inhibit bacterial attachment, the surface of a coating must be hydrophobic. To accomplish this, coatings contain fluoropolymers and organosilicone compounds that have very low surface energies. Therefore, they do not allow the collection of liquid water and hence are not favourable surfaces for bacterial settlement. There are also many suitable bactericides and fungicides such as small molecule antibiotics, quaternary salts ("quats"), chloramines, or triazines that can be included in a coatings formulation. However, compounds that are not bound to the backbone of the principle coating resin can leach out over time, greatly reducing their useful life.

Biocidal polymers contain active functional groups such as quaternary amines, various quinolone carboxylic acid derivatives such as Norfloxacin, or various N-halamines. These polymers may be classified as "biocide release," or "non-contact kill". Biocide release systems are available commercially [3-5]. Meanwhile, inorganic compounds such as zinc oxide, titanium dioxide and silver compounds may be dispersed in ordinary polymers to afford a "contact kill" class of antimicrobial coatings [6-8].

SUPERHYDROPHOBIC, SELF-CLEANING, EASY-TO-CLEAN, AND ANTI-ICING

In general, superhydrophobic surfaces can be achieved by two distinct methods: a texture induced method, or by formulation design, using low surface energy materials (*Figure 1*). The textured surfaces can be of either nanostructure; microstructure or hierarchical structures.

Hierarchical structure nanoparticles have been prepared by *Ming et al.* [9], and were then aligned in an epoxy matrix, leading to a dual-scale structured surface. Further modification of the surface with polydimethyl siloxane rendered the surface superhydrophobic, as evidenced by its high contact angle of 165°. Electrochemical polymerization has also been used to incorporate fluorinated hydrophobic or hydrocarbon groups onto monomers to obtain superhydrophobic films. *Yan et al.* [10] developed superhydrophobic polypyrrole films on a conducting surface. By simply adjusting electrochemical potential, the film surface demonstrated switchable wettability between superhydrophobicity and superhydrophilicity. Superhydrophobic coatings can also be prepared simply by incorporating speciality fluoropolymers, organosilicone compounds, or their combination, in a typical coating formulation.

SELF-STRATIFYING COATINGS

Self-stratifying coatings have potential technological and economic advantages: instead of applying two distinct layers of coatings, one could apply a self-stratifying coating that phase separates into two distinct layers with different concentration of resins and pigments upon drying or curing. The most simplistic approach is to blend immiscible materials in common solvents, or a mixture of solvents,

RESULTS AT A GLANCE

- Coatings can have functionality beyond their primary function of protection and decoration of substrates.
- Functional coatings are divided into two classes: those with intrinsic functionality and those that are extrinsic (responsive to external triggering mechanisms).
- The underlying physical and/or chemical processes are detailed for anti-microbial coatings, superhydrophobic coatings, self-stratifying coatings, photochromic coatings, self-healing and self-repair coatings, and thermochromic coatings.

thereby producing a homogeneous, thermodynamically stable liquid composition. In order to stratify, phase separation of the binder assembly needs to occur during, or immediately after the application to the substrate, as a result of evaporation of the common solvents, or reactions between the polymers where a latent curing catalyst and high temperature have been used.

Conceptually, in coatings containing all the necessary ingredients, four types of forces, either singularly, or in combination, can drive stratification: solvent/water evaporation, surface tension gradient, substrate wetting forces, and kinetically controlled reactions.

Incompatible polymers can also crosslink at two distinct rates, times, and under different temperatures. Examples of such systems are the reaction of epoxy resin with a thiol crosslinking agent and a typical reaction of a polyester/acrylic resin with either isocyanate compounds, or a melamine formaldehyde curing agent (*Figure 2*).

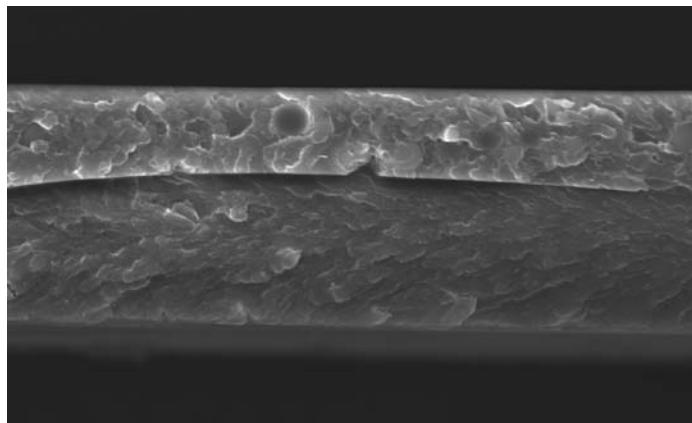
Thus, similar to a thermoplastic system, it is conceivable that one of the polymers is selected from the low surface energy class such as fluorine-modified acrylic/polyester/vinylether polyols while the other polymer is from the class of high surface energy materials such as epoxies or acrylic resins. *Baghdachi et al.* [11-14] have investigated and prepared prototype polyurethane self-stratifying coatings that phase separate into a colour coat and a clear coating in one application and process (*Figure 3*).

PHOTOCROMIC COATINGS

The most recognisable and one of the oldest extrinsic photochromic (stimuli responsive) commercial materials is the "Transitions" lens used in eye glasses. These are lenses made of glass or polycarbonate, containing photochromic materials, i.e., molecules of silver halides, that respond to light.

They are transparent to visible light without a significant ultraviolet component, which is normal for artificial lighting. When exposed to ultraviolet (UV) rays, as in direct sunlight, the molecules undergo a chemical process that causes them to change shape and absorb a significant percentage of the visible light, i.e., they darken. This process is reversible; once the lens is removed from strong sources of UV rays, the silver compounds return to their transparent state. Plastic photochromic lenses and coatings use organic photochromic molecules such as oxazines and naphthopyrans to achieve the reversible darkening effect.

Figure 3: SEM image of self-stratified coating.



SELF-HEALING AND SELF-REPAIR COATINGS

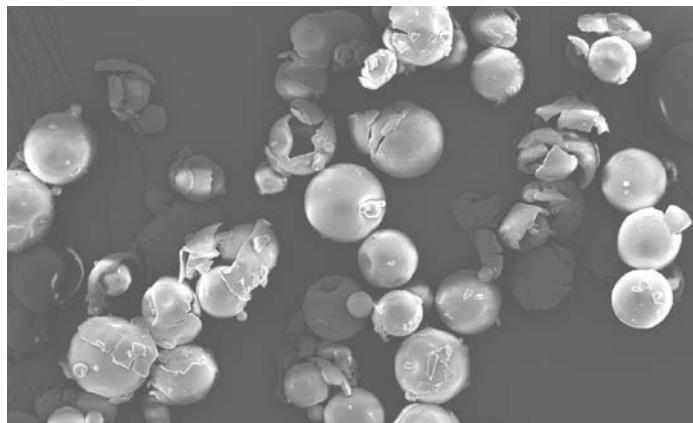
The durability of man-made materials is often limited by the absence of built-in "self-healing" mechanisms. Polymers have a finite lifetime; their inherent properties degrade with age [15]. The traditional approach for maintaining the predefined properties of polymers and coatings has been to include certain additives in the coating formulation that reduce the impact of environmental stress and natural fatigue. However, additives may also become fugitive materials, react, or interact with other coating ingredients, migrate out, or deplete over time and under adverse environmental service conditions [16].

The concept of healing polymers was established in the 1980s, but the presentation of self-healing polymer composites by *Dry* in 1993, followed by the well-cited *White* publication in 2001, inspired world-wide interest in these materials. Self-healing and self-repair concepts, using both organic and inorganic materials, have since been applied to composites, plastics, concrete, adhesives, and artificial skin [17-21]. A self-healing mechanism that can act repeatedly and infinitely to repair damaged coatings cannot, currently, be achieved.

However, coatings can be designed and formulated that can reduce the extent of the damage, thereby increasing the longevity of such functional coatings. In general, there are two major approaches to self-healing coatings; one is through polymer flow, alignment, realignment and bond formation/breakage; the other is by responsive additive materials. Both approaches still require a certain triggering mechanism. The method of thermally reversible crosslinking in composites was introduced in 2002 using Diels-Alder based cycloaddition of polymer chains containing multi-furan and multi-maleimide functionalities [22]. More recently, thermal repair of composites using epoxy compounds were demonstrated [23]. *Esteves et al.* [24] developed polyurethane polyester by exploring differences of energy as the driving force to repair the surface damage.

Noncovalent bond formation has been explored by *Sijbesma et al.*, in which supramolecular networks based on quadruple hydrogen bonding, ureido-pyrimidinone moieties, in response to local stress, align and repair the damage [25]. Responsive additive materials in the form of capsules containing various types of healing agents can also be included in an appropriate coating formulation. These may be triggered to offload the healing agents, reacting with coating ingredients, water, or trapped gasses, or to solidify; thereby repairing the damage. *Baghdachi et al.*, [16] developed and discussed the formulation and properties of self-healing polyurethane coatings that are triggered by the elements of weathering, i.e., excessive humidity, heat and environ-

Figure 4: SEM images of micro capsules containing healing agent.



mental light. Schematic representation of healing agent containing capsules is shown in Figure 4.

THERMOCHROMIC COATINGS

Reflective and solar radiation absorbing coatings are designed to change their optical properties according to the outdoor temperature and solar radiation levels. The main properties of a material that controls its surface temperature are the solar reflectance and the infrared emittance. Increased values of reflectance and/or emittance result in lower surface temperatures. This property can be described and analysed by thermochromism.

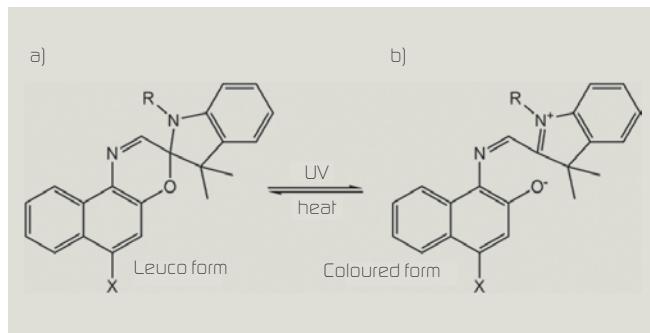
Thermochromism is the property of organic or inorganic substances that change colour, or spectral properties, due to a change in temperature, e.g., heating or cooling. In intrinsically reversible organic thermochromic systems, heating above a defined temperature causes a change in colour from darker to lighter tones. This transition is achieved by a thermally reversible transformation of the molecular structure of the pigments that produces a spectral change of visible colour. When temperature decreases below the colour-changing point, the system returns to its thermally stable state [26].

Thermochromic coatings are composed of non-infrared light absorbing polymers (ordinary polymers), typical coating additives, solvents/water and thermochromic pigments. The two common thermochromic pigments are based on liquid crystals and leuco dyes (Figure 5). Thermochromic dyes are based on mixtures of leuco dyes with other suitable chemicals, displaying a colour change (usually between the colourless leuco form and the coloured form) as a function of temperature. The dyes are rarely applied on materials directly; they are usually introduced in the form of microcapsules with the mixture sealed inside. Liquid crystals are used in precision applications, as their responses can be engineered to accurate temperatures, but their colour range is limited by their principle of operation. Leuco dyes allow wider range of colours to be used, but their response temperatures are more difficult to set with accuracy. ↗

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Figure 5: Representative chemical structure of leuco dye: (a) white form, (b) purple blue form.



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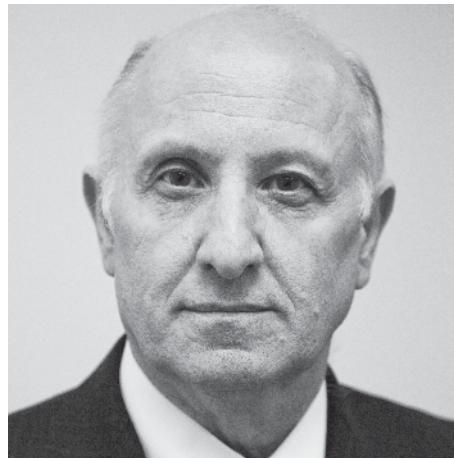
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VINCENTZ

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"In reality, functional coatings are the result of a need for multi-functionality."

3 questions to Dr Jamil Baghdachi

Where do you see limits on functionalities?

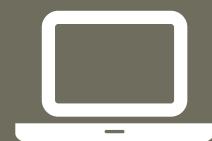
Functionalities are only limited based on our imagination. Considering the most recent developments, no particular road blocks are anticipated. Functionalities such as touch sensitivity and antimicrobial did not even exist 15 years ago.

What functionalities are currently researched on?

In general, multi-functionalities and property switching are being researched more often than others. More practical applications for shape-memory, self-healing, self-stratifying, and stimuli responsive coatings are heavily focused on.

Do you think that multi-functionality is of increasing importance in the coatings industry?

In reality, functional coatings are the result of a need for multi-functionality. Multifunctional coatings are sustainable, efficient and economical. They provide the basic functions of coatings and achieve results that cannot be attained any other way.



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ERRATUM

Unfortunately, the first sentence of the lead text by Dr Christiana Kremer in our section "Product overview" in the December issue (page 20) was not accurate. Please find here the correct sentence: "Epoxy based coatings can be formulated to have an excellent high chemical and mechanical resistance, by a given strong adhesion to metal."